



PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

GREGG M. SKLEDAR  
KENNETH D. HOPE

Serial No.: 09/343,334

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For: POLYALPHAOLEFINS WITH IMPROVED  
OXIDATIVE STABILITY AND THE  
PROCESS OF MAKING THEREOF

Group Art Unit: 1764

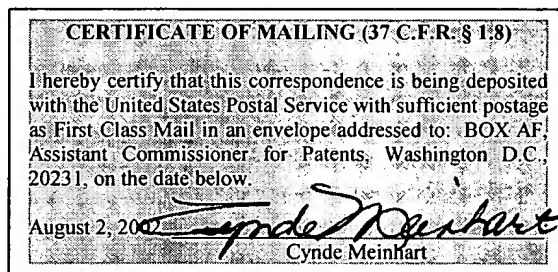
Examiner: N. Preisch

Attorney Docket: 2039.010700/RFE

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APPEAL BRIEF

**BOX AF**  
Assistant Commissioner of Patents  
Washington, D.C. 20231



Sir:

Applicants hereby submit an original and two copies of this Appeal Brief to the Board of Patent Appeals and Interferences in response to the final Office Action dated March 20, 2002. The fee for filing this Appeal Brief is \$320, and is attached hereto.

If the check is inadvertently omitted, or should any additional fees under 37 C.F.R. §§ 1.16 to 1.21 be required for any reason relating to the enclosed material, or should an overpayment be included herein, the Assistant Commissioner is authorized to deduct or credit said fees from or to Williams, Morgan & Amerson, P.C. Deposit Account No. 50-

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## I. REAL PARTY IN INTEREST

The assignee of this application is Chevron Chemical Company LLC, and the real party in interest is its successor in interest, Chevron Phillips Chemical Company LP.

## II. RELATED APPEALS AND INTERFERENCES

No other appeals or interferences known to Appellant will directly affect, be directly affected by, or have a bearing on the Board's decision in this appeal.

## III. STATUS OF THE CLAIMS

Claims 1-28 have been rejected and are the subject of this appeal.

## IV. STATUS OF AMENDMENTS

No amendments have been filed in this application after the final rejection. All previous amendments have been entered.

During preparation of this brief, applicant noticed what could be construed to be a typographical error in claims 27 and 28. These claims use the term "PAO," which is clearly intended to mean "polyalphaolefin." If correction is deemed necessary by the Office, Applicant will correct this typographical error by amending either claims 27-28 or claim 1 after this appeal is resolved.

## V. SUMMARY OF THE INVENTION

The present invention relates to polyalphaolefins (PAOs) having high oxidative stability and methods of producing the same. The methods involved hydrogenating a PAO to an extent that, in some embodiments, it has a Bromine Index of less than 200 mg bromine per 100 g of PAO. The term "Bromine Index," as used in the claims, is determined by a test designated "K801" as set forth in the present specification at p. 5, line 26 to p. 6, line 9.

Polyalphaolefins are synthetic oils which are useful as engine and gear lubricants and greases, as well as in other similar applications (p. 1, lines 13-21). It is known in the art to manufacture polyalphaolefins by oligomerizing linear alpha olefins, hydrogenating unsaturated moieties, and fractionating to obtain a desired product state (p. 1, lines 22-24). Commonly used alpha olefins include 1-decene, 1-dodecene, and 1-tetradecene (p. 1, line 24-p. 2, line 2). These compounds have the general structure  $\text{CH}_2=\text{CHCH}_2(\text{CH}_2)_n\text{CH}_3$ . For 1-decene, 1-dodecene, and 1-tetradecene, n is 6, 8, and 10, respectively.

Oligomerizing linear alpha olefins typically proceeds through a Friedel-Crafts-type reaction, as is well known to one of ordinary skill in the art. In this reaction, linear alpha olefins are exposed to a catalyst complex comprising, typically, boron trifluoride and a protic promoter (often an alcohol) under appropriate conditions. Oligomerization primarily forms single bonds between alpha olefin units, but leaves at least one double bond within each oligomer. Also, the reaction leads to backbone rearrangement and migration of double bonds. Therefore, in an oligomerized linear alpha olefin, the number of double bonds (which may also be referred to as the "degree of unsaturation") will be greater than zero.

It is desirable to increase the saturation (i.e., to reduce the degree of unsaturation or the number of double bonds) of a polyalphaolefin sample, in the expectation that increasing the saturation would render the polyalphaolefin more stable to oxidation and heat (p. 2, lines 8-10). Increasing the saturation of a polyalphaolefin can be achieved by hydrogenation (p. 2, lines 8-10). One of ordinary skill in the art will recognize that hydrogenation involves the reaction of the polyalphaolefin with hydrogen in the presence of a catalyst under conditions wherein the hydrogen is added to the carbons sharing a double bond (i.e.,  $\text{H}_2 + \text{RCH}=\text{CHR}' \rightarrow \text{RCH}_2-\text{CH}_2\text{R}'$ , wherein the single (-) and double (=) bonds are between the carbon atoms and R and R'

independently represent any organic moiety). Reaction conditions relevant to hydrogenation include temperature, reactant and catalyst concentrations, state of reactants (liquid, gas, solid, solute, etc.), and the nature of solvent, if any, among others. One of ordinary skill in the art will recognize that the extent to which hydrogenation proceeds depends on the duration of reaction (a longer duration will tend to lead to a higher degree of saturation), the reactivity of the reactants, and the nature of the catalyst, among other parameters.

It is useful to have a technique for measuring the degree of unsaturation in a hydrocarbon sample. One such technique is the so-called "Bromine Number" standard, published by the American Society for Testing and Materials (ASTM), West Conshohocken, PA, as D 1159-98<sup>†</sup>. A copy of this standard is attached hereto as Appendix B. In this standard, bromine (which adds across carbon-carbon double bonds under the test conditions) is titrated against a sample of the unsaturated hydrocarbon. The test method reports the sample's Bromine Number, which is defined as the number of grams of bromine that react with 100 g of the sample under test conditions (ASTM D 1159-98, paragraph 3.1.1). However, the standard has several limitations, as it itself recognizes. First, the test method is not satisfactory for normal alpha-olefins (ASTM D 1159-98, paragraph 1.1.2). Second, for samples with Bromine Number less than 1.0, a more precise measure for bromine-reactive constituents (i.e., carbon-carbon double bonds) can be obtained by use of ASTM D 2710, and if the Bromine Number is less than 0.5, ASTM D 2710 *must* be used (ASTM D 1159-98, paragraph 1.3).

ASTM D 2710-99 is the so-called "Bromine Index" standard. A copy of this standard is attached hereto as Appendix C. Similarly to the Bromine Number standard, in this standard, bromine (which adds across carbon-carbon double bonds under the test conditions) is titrated

against a sample of the unsaturated hydrocarbon. The test method reports the sample's Bromine Index, which is defined as the number of milligrams of bromine that react with 100 g of the sample under test conditions (ASTM D 2710-99, paragraph 3.1.1). However, despite the similarities of the two standards, *"the practice of using a factor of 1000 to convert bromine number to bromine index is not applicable for [values of Bromine Number less than 1.0]"* (ASTM D 1159-98, paragraph 1.3, emphasis added). One of ordinary skill in the art will recognize the correctness of this teaching from consideration of the nature of titration. In a titration, a solution is added dropwise to a sample until an indicator (e.g., sample electrical potential) reaches an established threshold value. All other things being equal, a more precise measurement will be achieved by use of a more dilute solution. The Bromine Index standard calls for a 0.05 N bromine solution, whereas the Bromine Number standard calls for a 0.25 M as Br<sub>2</sub> bromine solution.

Also, Applicants report a number of shortcomings with both the Bromine Number and Bromine Index standards, specifically, "[t]he chemical structure of PAO [polyalphaolefin] differs from ... petroleum hydrocarbons [e.g., cumenes, reformates, and kerosenes, for which the Bromine Index method was originally developed] in terms of the degree of branching and therefore there is a greater steric hindrance to the bromination reaction for PAO. In addition, PAO is limited in solubility in the test solvent [described by ASTM D 2710-99, paragraph 7.3.6, as comprising 714 mL/L glacial acetic acid, 134 mL/L 1,1,1-trichloroethane or dichloromethane, 134 mL/L methanol, and 18 mL/L H<sub>2</sub>SO<sub>4</sub> (16.7 vol% in water)], which creates problems with accuracy and repeatability" (p. 5, lines 21-25). Applicants therefore modified the Bromine Index method by using isopropanol as an additional solvent, higher temperatures, the taking of blank

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<sup>†</sup> ASTM standards are typically identified by an alphanumeric code, such as "D 1159" or "D 2710." A suffix comprising a hyphen and a two-digit number, such as "-98" or "-99," indicates the year in the twentieth century in

measurements for each solvent batch, and using an electrometric end point titration apparatus from Mettler (Mettler-Toledo, Inc., Columbus, OH) (p. 6, lines 1-7). The Modified Bromine Index method was designated K801 (p. 5, lines 26-27).

Techniques for measuring oxidative stability of a hydrocarbon sample include ASTM D 2272-98, which may herein be referred to as the "RBOT" test method. A copy of this standard is attached hereto as Appendix D. In this test method, the sample, water, and copper catalyst coil are placed in a vessel which is charged with oxygen to a gage pressure of 620 kPa, and the method reports the amount of time in minutes required for the oxygen pressure to drop by 175 kPa from an established plateau or a peak. Another technique for measuring oxidative stability of a hydrocarbon sample is the Lube Oil Oxidator test, for which no standard has yet been established by ASTM, to the best of applicants' knowledge. This test measures oxygen uptake and reports the amount of time until 1 L of oxygen is consumed by the sample under defined test conditions. A third technique is the Penn State Microoxidation method discussed by Gunsell et al., *J. Soc. Tribologists Lubr. Engrs.* 43(8):629-635 (1987) (hereinafter "Gunsell"). A copy of Gunsell is attached hereto as Appendix E.

In one embodiment, the present invention is a method of producing a high oxidative stability polyalphaolefin comprising the step of hydrogenating polyalphaolefin to a level of hydrogenation in which a Bromine Index of less than 200 mg Bromine per 100 gram sample of polyalphaolefin is achieved (claim 1). As stated above, generally, by reducing the degree of unsaturation of a polyalphaolefin, the oxidative stability of the polyalphaolefin is increased. In further embodiments, the polyalphaolefin is hydrogenated to a Bromine Index of less than 100 (claim 2), less than 50 (claim 3), or less than 25 (claim 4).

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which the most recent version of the standard was promulgated.

In another embodiment, the method of claim 1 further comprises distilling the polyalphaolefin to remove impurities prior to hydrogenation (claims 5 and 27). In a further embodiment, the polyalphaolefin is hydrogenated prior to distilling (i.e., the method comprises first hydrogenating, distilling, and second hydrogenating) (claims 9 and 28).

In yet another embodiment, the present invention is a lubricant composition comprising a polyalphaolefin having a Bromine Index less than 200 (claim 13). In further embodiments, the lubricant composition is a specific lubricant, such as an engine oil or a gear lubricant, among others (claims 17-24).

In still another embodiment, the present invention is a method of producing a composition comprising a highly oxidatively stable polyalphaolefin and a diphenylamine antioxidant, comprising hydrogenating the polyalphaolefin to an RBOT level of at least 2200 minutes and adding the diphenylamine to the polyalphaolefin (claim 25). In yet another embodiment, the present invention is a method of producing a highly oxidatively stable polyalphaolefin, comprising hydrogenating the polyalphaolefin to a Lube Oil Oxidator level of at least 45 hr under specific conditions (claim 26).

The state of the prior art can be seen in Gunsel (discussed at p. 3, lines 17-28). Gunsel evaluated two polyalphaolefin samples. Sample A had a stated Bromine Index of 1323, and the sample B had a stated Bromine Index of 2 (p. 3, lines 19-21). (One of ordinary skill in the art will recognize that "stated Bromine Index" refers to a Bromine Index determined according to ASTM D 2710-99). Gunsel also reported the oxidative stability of the two samples.

Applicants subsequently prepared two polyalphaolefin samples according to the present invention for comparison with the prior art samples of Gunsel (p. 6, lines 10-26). Sample 1 had a Bromine Index as measured by K801 (hereinafter "modified Bromine Index") of 433, and

sample 2 had a modified Bromine Index of 0.95. Both samples 1 and 2 had better oxidative stability than Günsel's sample B (p. 15, line 11-p. 16, line 14, and Figure). Given the assumption that the oxidative stability of a polyalphaolefin correlates with the degree of saturation of the polyalphaolefin, then one of ordinary skill in the art would conclude Günsel's sample B, with a stated Bromine Index of 2, in fact had a greater degree of unsaturation than Applicants' sample 1, which had a modified Bromine Index of 433 (p. 16, lines 7-14). This indicates that Günsel's sample B did not have a modified Bromine Index of less than 200 and thus the present claims do not read on Günsel. This is confirmed by the observation that, although Günsel is of record in this case, the Examiner never argued that Günsel would provide the basis for a prior art rejection of any of the pending claims.

## VI. ISSUES ON APPEAL

A. Are claims 13-24 unpatentable under 35 U.S.C. § 102(b) as being anticipated by Wu et al., U.S. Pat. No. 5,276,227 (hereinafter "Wu")?

B. Are claims 1-8, 10-12, and 27 unpatentable under 35 U.S.C. §103(a) in view of Sauer, U.S. Pat. No. 3,113,167 (hereinafter "Sauer") and Wu?

C. Are claims 1-4, 6-12, 26, and 28 unpatentable under 35 U.S.C. §103(a) in view of Cupples et al., U.S. Pat. No. 4,282,392 (hereinafter "Cupples") and Wu?

D. Is claim 25 unpatentable under 35 U.S.C. §103(a) in view of either Cupples, Wu, and Fear, U.S. Pat. No. 2,980,603 (hereinafter "Fear"); Sauer, Wu, and Fear; or Cupples and Wu, Sauer and Wu, and Fear?

## VII. GROUPING OF THE CLAIMS

Claims 1-4 can be considered as a first group.

Claims 5-8 and 27 can be considered as a second group.



Claims 9-12 and 28 can be considered as a third group.

Claims 13-24 can be considered as a fourth group.

Claim 25 can be considered as a fifth group.

Claim 26 can be considered as a sixth group.

The claims in each of the above groups stand or fall together. The reasons why these six groups are separately patentable are explained below in the Argument.

## VIII. ARGUMENT

### A. Novelty of claims 13-24 over Wu

The Examiner contends that claims 13-24 are anticipated by Wu. Wu teaches polymers derived at least in part from C<sub>3</sub>-C<sub>5</sub> alphaolefin oligomers (Abstract and col. 3, lines 10-15). The polymers are useful in high-shear-stability viscosity-index-improver lubricant compositions (Abstract and col. 3, lines 10-15). Also, Wu states, “all references to properties of oligomers or lubricants of the present invention refer as well to products of low unsaturation, as characterized by low bromine number, usually lower than 4” (col. 3, lines 48-51). The Examiner alleges that Wu therefore discloses a lubricant composition comprising a polyalphaolefin having a Bromine Index of less than 200.

First, it should be clear that the term “Bromine Index,” as recited by claims 13-24, refers to bromine indices determined by the modified Bromine Index method, K801. The K801 method was first reported in the present application (p. 5, line 26 to p. 6, line 9). Therefore, on the face of both claims 13-24 and the cited passage from Wu, Wu does not recite every element of the pending claims.

Instead, the Examiner has based the rejection on a reading of Wu’s “bromine number[,]  
usually lower than 4” as disclosing polyalphaolefins with a range of saturations from complete

saturation to being saturated to an extent which is quantifiable as a Bromine Number of 4. If this reading of Wu were accurate, then Wu's polyalphaolefins' range of saturations would encompass the modified Bromine Index of less than 200 recited by claims 13-24. However, one of ordinary skill in the art would recognize that this reading of Wu is *not* accurate.

First, according to MPEP 2131.03, a reference can anticipate a claimed range only if the reference provides a specific example within the claimed range or discloses a range which touches, overlaps, or lies within the claimed range. Clearly, Wu does not provide a specific example of a polyalphaolefin with a degree of saturation quantifiable as a Bromine Index of less than 200 as measured by K801. As to whether Wu discloses a range within the claimed range, the Examiner only made the bald statement that "bromine number usually lower than 4" is equivalent to a bromine number of 0-4. The phrase "bromine number usually lower than 4" is a set comprising a large number of possible ranges. For example, members of the set include bromine number ranges 3-4, 2-4, and 1-4, among others. One of ordinary skill in the art would recognize these three exemplary members of the set would not touch, overlap, or lie within the claimed range of Bromine Indices. Although other members of the set may, at first glance, touch, overlap, or lie within the claimed range, Wu provides no guidance to determine which member of the set of bromine number ranges was in fact achieved by Wu. Because Wu discloses an upper limit which is far higher than the claimed range, but no lower limit, Wu fails to disclose a range which touches, overlaps, or lies within the claimed range. The Examiner recognized this in Paper 17, p. 2, wherein she stated "It is maintained that Wu *suggests* a bromine index within applicants' claimed range" (emphasis added). Use of the word "suggests" indicates the Examiner recognized Wu does not *disclose* the claimed range, either explicitly or inherently. Therefore, Wu cannot anticipate claims 13-24.

Further, Wu does *not* suggest the presently claimed modified Bromine Index of less than 200, for a number of reasons. First, one of ordinary skill in the art would recognize the limitations of the bromine number measurement performed by Wu. As discussed above, the Bromine Number standard, ASTM D 1159-98, has poor precision for samples with apparent Bromine Number of 1.0 or less, and *must not be used* with samples with apparent Bromine Number of 0.5 or less (Appendix B, paragraph 1.3). This indicates that one of ordinary skill in the art would conclude that Wu's teaching of "bromine number usually lower than 4" cannot precisely define any Bromine Number of less than about 0.5 measured according to ASTM D 1159, let alone any modified Bromine Number measured according to K801.

Second, even if, accepted solely for the sake of argument, Wu could be construed to define a Bromine Number of less than 0.2 (and this Bromine Number could be converted to a Bromine Index of 200 by use of a factor of 1000, which is strictly *not applicable* according to ASTM D 1159-98), Applicants demonstrate that a polyalphaolefin reported by the art to have a bromine index of 2 (as measured by ASTM D 2710-99) most likely had a degree of unsaturation that would have been quantified as a modified Bromine Index of at least 433 according to the K801 protocol developed by Applicants. As stated above, Gunsel reported a polyalphaolefin (sample B) with a bromine index of 2, but sample B showed poorer oxidative stability than Applicants' sample 1. Sample 1 had a modified Bromine Index (i.e., a Bromine Index measured according to K801) of 433. Given the general rule that oxidative stability correlates with degree of saturation, the poorer oxidative stability of sample B relative to Applicants' sample 1 would lead one of ordinary skill in the art to conclude that sample B had a lesser degree of saturation than sample 1. In other words, sample B's modified Bromine Index would most likely be at least 433, and not 2. From this, one of ordinary skill in the art would conclude that, even if Wu's

“bromine number usually lower than 4” could be construed to cover polyalphaolefins with bromine indices of 0-2 as measured by ASTM D 2710-99, there would be no justification for assuming these polyalphaolefins would have modified Bromine Indices of less than 200 as measured by the K801 protocol and recited by claim 13.

This conclusion is supported by consideration of ASTM D 2710-99 and the chemistry of bromine. Bromine ( $\text{Br}_2$ ) has a molecular weight of 159.808 g/mol. Gunsel sample B's bromine index of 2 mg per 100 g polyalphaolefin therefore corresponds to 0.0125 mmol  $\text{Br}_2$  per 100 g polyalphaolefin. The amount of polyalphaolefin in Gunsel's sample B is not known, but was plausibly approximately 10 g. Therefore, a total of about 0.00125 mmol  $\text{Br}_2$  was used in determining the bromine index of Gunsel's sample B. Assuming the bromine solution was added in drops of 0.02 mL, each drop of 0.05 N bromine solution contained 0.001 mmol  $\text{Br}_2$ . Therefore, only about 1-2 drops of bromine solution would give the bromine index of 2 reported by Gunsel for sample B. For a hypothetical sample of Wu's with a bromine index of 0, 1 drop of bromine solution would still be required to determine that the sample had no unsaturation. As a result, and irrespective of the reproducibility of the measurements of Gunsel, the precision of ASTM D 2710-99 indicates that a bromine index of 2 as measured by this standard cannot be distinguished from a bromine index of 0. Therefore, one of ordinary skill in the art would conclude a hypothetical sample of Wu's with a bromine index of 0 would be about as unsaturated as Gunsel's sample B, and as stated above, Gunsel's sample B most likely had a modified Bromine Index of at least 433, which is greater than the Bromine Indices recited by the present claims. Therefore, a hypothetical sample of Wu with bromine index of 0 measured according to ASTM D 2710-99 would not inherently have a modified Bromine Index of less than 200.

Further, the Examiner argued that one of ordinary skill in the art, in light of Wu, would be motivated to hydrogenate a sample to as low a bromine index as possible. However, hydrogenation carries expenses for hydrogen, catalyst, energy, and time, and so the benefit of hydrogenation must be weighed against the costs. Wu does not provide insight to one of ordinary skill in the art to weigh the various benefits and costs, and thus, considered strictly for the sake of argument, Wu does not lead one of ordinary skill in the art to pursue a degree of saturation indicated by bromine numbers as measured by ASTM D 1159-98 of less than 1.0, less than 0.5, or less than 0.2, let alone modified Bromine Indices of 200 or less as measured by K801. This is especially true given that Wu fails to define any degree of saturation other than “usually lower than 4.” If pursuit of very low levels of unsaturation (i.e., very low bromine numbers or bromine indices) is highly beneficial, one of ordinary skill in the art would expect Wu to report the lowest levels of unsaturation generally reached by the authors in their work. For example, if Wu consistently produced polyalphaolefins with bromine numbers of less than 2, one would expect Wu to affirmatively state this fact. One of ordinary skill in the art will draw the conclusion from Wu that Wu consistently hydrogenated polyalphaolefins to a bromine number of about 4 but greater than 3.

Further, even if Wu were to report bromine numbers much lower than 4, the discussion above regarding Günsel and its applicability to Wu as expressing the state of the art at the time of Wu’s invention indicates that any extent of hydrogenation suggested by Wu would in fact not be to an extent necessary to prepare polyalphaolefins with a modified Bromine Index of less than 200.

Therefore, the rejection of claims 13-24 as being anticipated by Wu should be reversed.

B. Nonobviousness of claims 1-8, 10-12, and 27 over Sauer in view of Wu

The Examiner contends claims 1-8, 10-12, and 27 are unpatentable over Sauer in view of Wu. Sauer teaches a process for polyalphaolefin production, involving a distillation step followed by a polymer hydrogenation step (col. 7, lines 43-45; col. 8, lines 43-45). Although Sauer states “reaction times of about 8 hours have been used to insure complete hydrogenation of the polymer” (col. 6, lines 14-15), Sauer does not quantify the extent to which hydrogenation is performed. The Examiner cited Wu as supplementing Sauer by quantifying the extent of hydrogenation as proceeding to a “bromine number usually lower than 4” as described above.

Claims 1-4 recite a method of producing a high oxidative stability polyalphaolefin comprising hydrogenating polyalphaolefin to a Bromine Index of less than 200. Sauer teaches hydrogenating polyalphaolefin. However, neither reference, nor their combination, teaches or suggests hydrogenating polyalphaolefin to a modified Bromine Index of less than 200.

Wu has been discussed above, with the conclusion that Wu’s teaching of polyalphaolefins with “bromine number usually lower than 4” does not teach polyalphaolefins with a modified Bromine Index (i.e., a Bromine Index measured according to K801) of less than 200. Within that discussion, it was pointed out that even if Wu were assumed to report a polyalphaolefin with a bromine index (as measured by ASTM D 2710-99) of 0, that Gunsels’ sample B, with a reported bromine index of 2, was in fact more unsaturated than Applicants’ sample 1, which had a modified Bromine Index of 433. Given the imprecision of ASTM D 2710-99 in distinguishing between bromine indices of 2 and 0, for the reasons discussed above, one of ordinary skill in the art would conclude any hypothetical sample of Wu with a bromine index of 0 in reality would have a modified Bromine Index of at least 433 and thus the present claims would not read on the reference.

Regarding Sauer, even if “complete hydrogenation” were assumed to refer to a polyalphaolefin with a bromine index of 0, such a bromine index would have been measured according to ASTM D 2710, and by the same reasoning as applied to Wu in view of the state of the art as manifest in Gunsel, such a polyalphaolefin of Sauer would presumably have a modified Bromine Index of at least 433, and the present claims would not read on Sauer also. Because neither reference teaches or suggests a polyalphaolefin having a Bromine Index of less than 200, their combination cannot either.

Claims 5-8 and 27 differ from claims 1-4 by reciting that the polyalphaolefin is distilled prior to hydrogenating to a Bromine Index of less than 200. Although Sauer teaches distilling a polyalphaolefin prior to hydrogenation, neither Sauer, Wu, nor their combination teaches or suggests hydrogenating to a Bromine Index of less than 200, for the reasons discussed above.

Claims 10-12 differ from claims 5-8 and 27 by reciting that the polyalphaolefin is hydrogenated prior to distilling and hydrogenating to a Bromine Index of less than 100. Neither Sauer nor Wu teaches or suggests hydrogenating prior to distilling and hydrogenating, and therefore their combination cannot either. In addition, the limitation of hydrogenating to a Bromine Index of less than 100 is neither taught nor suggested by Sauer, Wu, or their combination, for the reasons set forth above.

Therefore, the rejection of claims 1-8, 10-12, and 27 as being obvious over Sauer in view of Wu should be reversed.

C. Nonobviousness of claims 1-4, 6-12, 26, and 28 over Cupples in view of Wu

The Examiner contends claims 1-4, 6-12, 26, and 28 are unpatentable over Cupples in view of Wu. Cupples teaches the hydrogenation of alphaolefin oligomers (col. 4, lines 4-8), and

subsequent removal of light fractions by flashing off from the hydrogenated product (col. 6, lines 2-3). Cupples does not teach a subsequent hydrogenation to a modified Bromine Index of less than 200. The Examiner cited Wu as teaching a subsequent hydrogenation to a “bromine number usually lower than 4.”

As stated above, Cupples does not provide a quantified or qualified statement of the extent of hydrogenation. Wu’s teaching of polyalphaolefins with a “bromine number usually lower than 4” has been discussed above as neither teaching nor suggesting polyalphaolefins with a modified Bromine Index (as measured according to K801) of less than 200. Claims 1-4 recite hydrogenating polyalphaolefins with a modified Bromine Index of less than 200. Because neither reference teaches or suggests hydrogenating polyalphaolefins to such an extent, their combination cannot teach or suggest such hydrogenation either.

Claims 6-8 differ from claims 1-4 by reciting distilling the polyalphaolefin prior to hydrogenating to a modified Bromine Index of less than 100. Cupples only teaches distillation after hydrogenation (col. 6, lines 2-3; col. 6, line 65-col. 7, line 1; col. 7, lines 23-25 and 58-61), and Wu is not cited as teaching distillation prior to hydrogenation. Therefore, there is no motivation to combine the teachings of these references to distill prior to hydrogenating. Further, neither Cupples nor Wu teaches nor suggests hydrogenation to a modified Bromine Index of less than 100, for the reasons discussed above, and therefore their combination cannot teach or suggest such hydrogenation either.

Claims 9-12 and 28 differ from claims 6-8 by reciting a process comprising first hydrogenating, distilling, and second hydrogenating to a modified Bromine Index of less than 200. In a similar argument to that regarding claims 6-8, there is no motivation to combine Cupples (which teaches hydrogenating followed by distilling) and Wu (which teaches



hydrogenating) to arrive at a method comprising first hydrogenating, distilling, and second hydrogenating to a modified Bromine Index of less than 200. Further, neither Cupples nor Wu teaches nor suggests hydrogenation to a modified Bromine Index of less than 200, for the reasons discussed above, and therefore their combination cannot teach or suggest such hydrogenation either.

Claim 26 differs from claims 1-4 by reciting hydrogenating a polyalphaolefin to a level of hydrogenation associated with a Lube Oil Oxidator level of at least 45 hr at pressures of 35 to 2500 psi. Neither Cupples nor Wu reports a Lube Oil Oxidator level for any polyalphaolefin sample prepared by either set of workers. Also, there is no teaching or suggestion in either reference that such a Lube Oil Oxidator level was achieved or would be desirable to be achieved. In the present Application at Table 1, p. 13, Applicants report samples with Lube Oil Oxidator levels of from 44-57 hr and modified Bromine Indices of 1.6-10. Given the correlation between degree of saturation and oxidative stability, and the conclusion that the polyalphaolefins of Wu would have modified Bromine Indices of at least 433, one of ordinary skill in the art would conclude the polyalphaolefins of Wu would have poorer oxidative stability than the samples with Lube Oil Oxidator levels of 44-57 hr. This is indicated by a sample reported in Table 1, p. 13, which has a modified Bromine Index of 433 and a Lube Oil Oxidator level of 16 hr. Therefore, neither Cupples, Wu, nor their combination teaches a process comprising hydrogenating to such a Lube Oil Oxidator level.

Therefore, the rejection of claims 1-4, 6-12, 26, and 28 as being obvious over Cupples in view of Wu should be reversed.

D. Nonobviousness of claim 25 over either Cupples, Wu, and Fear; Sauer, Wu, and Fear; or Cupples and Wu, Sauer and Wu, and Fear

Claim 25 is rejected as being unpatentable over either Cupples, Wu, and Fear; Sauer, Wu, and Fear; or Cupples and Wu, Sauer and Wu, and Fear. Cupples, Sauer, and Wu, either individually or in any combination, teach hydrogenating polyalphaolefins. The Examiner cited Fear as teaching the use of diphenylamine antioxidants in polyalphaolefin compositions (col. 5, lines 28-46).

Claim 25 recites hydrogenating polyalphaolefin to a level of hydrogenation which is associated with an RBOT level of at least 2200 min. The RBOT level is a measure of oxidative stability, and would thus be expected to be inversely correlated with modified Bromine Index. (In other words, a higher RBOT level is expected for a sample with a lower modified Bromine Index, relative to a second sample). This is indicated in the present application at Table 1, p. 13. The only polyalphaolefins with an RBOT level of at least 2200 min have modified Bromine Indices of 10 or less.

As described above, none of the polyalphaolefins of Cupples, Sauer, or Wu has been hydrogenated to a modified Bromine Index less than 433. Fear is also silent regarding the extent of hydrogenation suitable for production of an oxidation-resistant polyalphaolefin lubricant composition. As reported by Table 1, p. 13, polyalphaolefins with a modified Bromine Index of 433 or greater have RBOT levels of about 800 min to about 1300 min. Therefore, none of the references, alone or in any combination, teaches or suggests a method comprising hydrogenating polyalphaolefin to an RBOT level of at least 2200 min.

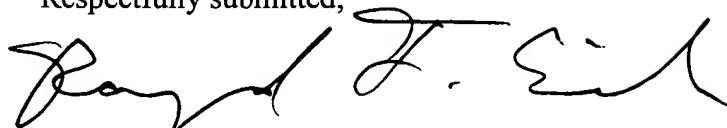
Therefore, the rejection of claim 25 over Cupples, Wu, and Fear; Sauer, Wu, and Fear; or Cupples and Wu, Sauer and Wu, and Fear should be withdrawn.

IX. CONCLUSION

The rejections of claims 1-28 should be reversed.

Please date stamp and return the enclosed postcard to evidence receipt of this document.

Respectfully submitted,

A handwritten signature in black ink, appearing to read 'Raymund F. Eich', written in a cursive style.

Raymund F. Eich  
Reg. No. 42,508

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August 2, 2002

## **APPENDIX A**

### **Claims Involved in This Appeal**

1. A method of producing a high oxidative stability polyalphaolefin comprising the step of hydrogenating polyalphaolefin to a level of hydrogenation in which a Bromine Index of less than 200 mg Bromine per 100 gram sample of polyalphaolefin is achieved.
2. A method according to claim 1 wherein a Bromine Index of less than 100 mg Bromine per 100 gram sample of polyalphaolefin is achieved.
3. A method according to claim 1 wherein a Bromine Index of less than 50 mg Bromine per 100 gram sample of polyalphaolefin is achieved.
4. A method according to claim 1 wherein a Bromine Index of less than 25 mg Bromine per 100 gram sample of polyalphaolefin is achieved.
5. A method according to claim 1 further comprising distilling the polyalphaolefin to remove impurities before the hydrogenating step.
6. A method according to claim 5 wherein a Bromine Index of less than 100 mg Bromine per 100 gram sample of polyalphaolefin is achieved.
7. A method according to claim 5 wherein a Bromine Index of less than 50 mg Bromine per 100 gram sample of polyalphaolefin is achieved.
8. A method according to claim 5 wherein a Bromine Index of less than 25 mg Bromine per 100 gram sample of polyalphaolefin is achieved.
9. A method according to claim 5 further comprising a preliminary hydrogenating of the polyalphaolefin before the distilling step.

10. A method according to claim 9 wherein a Bromine Index of less than 100 mg Bromine per 100 gram sample of polyalphaolefin is achieved.
11. A method according to claim 9 wherein a Bromine Index of less than 50 mg Bromine per 100 gram sample of polyalphaolefin is achieved.
12. A method according to claim 9 wherein a Bromine Index of less than 25 mg Bromine per 100 gram sample of polyalphaolefin is achieved.
13. A lubricant composition comprising a polyalphaolefin having a Bromine Index of less than 200 mg Bromine per 100 gram sample of polyalphaolefin.
14. A composition according to claim 13 wherein the composition has a Bromine Index of less than 100 mg Bromine per 100 gram sample of polyalphaolefin.
15. A composition according to claim 13 wherein the composition has a Bromine Index of less than 50 mg Bromine per 100 gram sample of polyalphaolefin.
16. A composition according to claim 13 wherein the composition has a Bromine Index of less than 25 mg Bromine per 100 gram sample of polyalphaolefin.
17. The composition of claim 13 wherein the composition is an engine oil lubricant.
18. The composition of claim 13 wherein the composition is a gear lubricant.
19. The composition of claim 13 wherein the composition is an hydraulic lubricant.
20. The composition of claim 13 wherein the composition is a compressor lubricant.
21. The composition of claim 13 wherein the composition is an aerospace jet lubricant.

22. The composition of claim 13 wherein the composition is a fiber optic cable gel.
23. The composition of claim 13 wherein the composition is a synthetic grease.
24. The composition of claim 13 wherein the composition is a dielectric fluid.
25. A method of producing a composition comprising a highly oxidatively stable polyalphaolefin and a diphenylamine antioxidant, comprising:
- hydrogenating polyalphaolefin to a level of hydrogenation in which an RBOT level of at least 2200 minutes is achieved; and
- adding the diphenylamine antioxidant to the polyalphaolefin, to form the composition.
26. A method of producing a highly oxidatively stable polyalphaolefin comprising the step of hydrogenating a polyalphaolefin to a level of hydrogenation in which a Lube Oil Oxidator level of at least 45 hours is achieved when pressures between 35 and 2500 psi are applied.
27. The method of claim 1, wherein the PAO is distilled prior to hydrogenation.
28. The method of claim 1, wherein the PAO is hydrogenated and distilled prior to the hydrogenation to a Bromine Index of less than 200.

## **APPENDIX A**

### **Claims Involved in This Appeal**

1. A method of producing a high oxidative stability polyalphaolefin comprising the step of hydrogenating polyalphaolefin to a level of hydrogenation in which a Bromine Index of less than 200 mg Bromine per 100 gram sample of polyalphaolefin is achieved.
2. A method according to claim 1 wherein a Bromine Index of less than 100 mg Bromine per 100 gram sample of polyalphaolefin is achieved.
3. A method according to claim 1 wherein a Bromine Index of less than 50 mg Bromine per 100 gram sample of polyalphaolefin is achieved.
4. A method according to claim 1 wherein a Bromine Index of less than 25 mg Bromine per 100 gram sample of polyalphaolefin is achieved.
5. A method according to claim 1 further comprising distilling the polyalphaolefin to remove impurities before the hydrogenating step.
6. A method according to claim 5 wherein a Bromine Index of less than 100 mg Bromine per 100 gram sample of polyalphaolefin is achieved.
7. A method according to claim 5 wherein a Bromine Index of less than 50 mg Bromine per 100 gram sample of polyalphaolefin is achieved.
8. A method according to claim 5 wherein a Bromine Index of less than 25 mg Bromine per 100 gram sample of polyalphaolefin is achieved.
9. A method according to claim 5 further comprising a preliminary hydrogenating of the polyalphaolefin before the distilling step.

10. A method according to claim 9 wherein a Bromine Index of less than 100 mg Bromine per 100 gram sample of polyalphaolefin is achieved.
11. A method according to claim 9 wherein a Bromine Index of less than 50 mg Bromine per 100 gram sample of polyalphaolefin is achieved.
12. A method according to claim 9 wherein a Bromine Index of less than 25 mg Bromine per 100 gram sample of polyalphaolefin is achieved.
13. A lubricant composition comprising a polyalphaolefin having a Bromine Index of less than 200 mg Bromine per 100 gram sample of polyalphaolefin.
14. A composition according to claim 13 wherein the composition has a Bromine Index of less than 100 mg Bromine per 100 gram sample of polyalphaolefin.
15. A composition according to claim 13 wherein the composition has a Bromine Index of less than 50 mg Bromine per 100 gram sample of polyalphaolefin.
16. A composition according to claim 13 wherein the composition has a Bromine Index of less than 25 mg Bromine per 100 gram sample of polyalphaolefin.
17. The composition of claim 13 wherein the composition is an engine oil lubricant.
18. The composition of claim 13 wherein the composition is a gear lubricant.
19. The composition of claim 13 wherein the composition is an hydraulic lubricant.
20. The composition of claim 13 wherein the composition is a compressor lubricant.
21. The composition of claim 13 wherein the composition is an aerospace jet lubricant.



22. The composition of claim 13 wherein the composition is a fiber optic cable gel.
23. The composition of claim 13 wherein the composition is a synthetic grease.
24. The composition of claim 13 wherein the composition is a dielectric fluid.
25. A method of producing a composition comprising a highly oxidatively stable polyalphaolefin and a diphenylamine antioxidant, comprising:
  - hydrogenating polyalphaolefin to a level of hydrogenation in which an RBOT level of at least 2200 minutes is achieved; and
  - adding the diphenylamine antioxidant to the polyalphaolefin, to form the composition.
26. A method of producing a highly oxidatively stable polyalphaolefin comprising the step of hydrogenating a polyalphaolefin to a level of hydrogenation in which a Lube Oil Oxidator level of at least 45 hours is achieved when pressures between 35 and 2500 psi are applied.
27. The method of claim 1, wherein the PAO is distilled prior to hydrogenation.
28. The method of claim 1, wherein the PAO is hydrogenated and distilled prior to the hydrogenation to a Bromine Index of less than 200.



## Standard Test Method for Bromine Numbers of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration<sup>1</sup>

This standard is issued under the fixed designation D 1159; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the Department of Defense.*

### 1. Scope

1.1 This test method<sup>2</sup> covers the determination of the bromine number of the following materials:

1.1.1 Petroleum distillates that are substantially free of material lighter than isobutane and that have 90 % distillation points (by Test Method D 86) under 327°C (626°F). This test method is generally applicable to gasoline (including leaded, unleaded, and oxygenated fuels), kerosine, and distillates in the gas oil range that fall in the following limits:

90 % Distillation Point, <sup>3</sup> C (°F)	Bromine Number, max <sup>2</sup>
Under 205 (400)	175
205 to 327 (400 to 626)	10

1.1.2 Commercial olefins that are essentially mixtures of aliphatic mono-olefins and that fall within the range of 95 to 165 bromine number (see Note 1). This test method has been found suitable for such materials as commercial propylene trimer and tetramer, butene dimer, and mixed nonenes, octenes, and heptenes. This test method is not satisfactory for normal alpha-olefins.

NOTE 1—These limits are imposed since the precision of this test method has been determined only up to or within the range of these bromine numbers.

1.2 The magnitude of the bromine number is an indication of the quantity of bromine-reactive constituents, not an identification of constituents; therefore, its application as a measure of olefinic unsaturation should not be undertaken without the study given in Annex A1.

1.3 For petroleum hydrocarbon mixtures of bromine number less than 1.0, a more precise measure for bromine-reactive

constituents can be obtained by using Test Method D 2710. If the bromine number is less than 0.5, then Test Method D 2710 or the comparable bromine index methods for industrial aromatic hydrocarbons, Test Methods D 1492 or D 5776 must be used in accordance with their respective scopes. The practice of using a factor of 1000 to convert bromine number to bromine index is not applicable for these lower values of bromine number.

1.4 The values stated in SI units are to be regarded as the standard. The inch-pound units given in parentheses are for information purposes only.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements, see Note 3 through Note 11.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

- D 86 Test Method for Distillation of Petroleum Products<sup>3</sup>
- D 1193 Specification for Reagent Water<sup>4</sup>
- D 1492 Test Method for Bromine Index of Aromatic Hydrocarbons by Coulometric Titration<sup>5</sup>
- D 2710 Test Method for Bromine Index of Petroleum Hydrocarbons by Electrometric Titration<sup>6</sup>
- D 5776 Test Method for Bromine Index Aromatic of Hydrocarbons by Electrometric Titration<sup>5</sup>

### 3. Terminology

#### 3.1 Definitions of Terms Specific to This Standard:

- 3.1.1 *bromine number*—the number of grams of bromine

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0D on Physical Methods.

In the IP, this test method is under the jurisdiction of the Standardization Committee.

Current edition approved Apr. 10, 1998. Published September 1998. Originally published as D 1159 – 51 T. Last previous edition D 1159 – 93.

<sup>2</sup> See Dubois, H. D., and Skoog, D. A., "Determination of Bromine Addition Numbers," *Analytical Chemistry*, Vol 20, 1948, pp. 624–7.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 06.04.

<sup>6</sup> *Annual Book of ASTM Standards*, Vol 05.02.

that will react with 100 g of the specimen under the conditions of the test.

#### 4. Summary of Test Method

4.1 A known weight of the specimen dissolved in the selected solvent (see Note 9) maintained at 0 to 5°C (32 to 41°F) is titrated with standard bromide-bromate solution. The end point is indicated by a sudden change in potential on an electrometric end point titration apparatus due to the presence of free bromine.

#### 5. Significance and Use

5.1 The bromine number is useful as a measure of aliphatic unsaturation in petroleum samples. When used in conjunction with the calculation procedure described in Annex A2, it can be used to estimate the percentage of olefins in petroleum distillates boiling up to approximately 315°C (600°F).

5.2 The bromine number of commercial aliphatic monoolefins provides supporting evidence of their purity and identity.

#### 6. Apparatus

6.1 *Electrometric End Point Titration Apparatus*—Any apparatus designed to perform titrations to pre-set end points (see Note 10) may be used in conjunction with a high-resistance polarizing current supply capable of maintaining approximately 0.8 V across two platinum electrodes and with a sensitivity such that a voltage change of approximately 50 mV at these electrodes is sufficient to indicate the end point. Other types of commercially available electronic titrimeters, including certain pH meters, have also been found suitable.

NOTE 2—Pre-set end point indicated with polarized electrodes provides a detection technique similar to the dead stop technique specified in previous versions of this test method.

6.2 *Titration Vessel*—A jacketed glass vessel approximately 120 mm high and 45 mm in internal diameter and of a form that can be conveniently maintained at 0 to 5°C (32 to 41°F).

6.3 *Stirrer*—Any magnetic stirrer system.

6.4 *Electrodes*—A platinum wire electrode pair with each wire approximately 12 mm long and 1 mm in diameter. The wires shall be located 5 mm apart and approximately 55 mm below the level of the titration solvent. Clean the electrode pair at regular intervals with 65 % nitric acid and rinse with distilled water before use.

6.5 *Buret*—Any delivery system capable of measuring titrant in 0.05 mL or smaller graduations.

#### 7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>7</sup> Other grades may be

used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type III of Specification D 1193.

7.3 *Acetic Acid, Glacial*—(Warning—See Note 3.)

NOTE 3—Warning: Poison, corrosive-combustible, may be fatal if swallowed. Causes severe burns, harmful if inhaled.

7.4 *Bromide-Bromate, Standard Solution (0.2500 M as Br<sub>2</sub>)*—Dissolve 51.0 g of potassium bromide (KBr) and 13.92 g of potassium bromate (KBrO<sub>3</sub>) each dried at 105°C (220°F) for 30 min in water and dilute to 1 L.

7.4.1 If the determinations of the bromine number of the reference olefins specified in Section 8 using this solution do not conform to the prescribed limits, or if for reasons of uncertainties in the quality of primary reagents it is considered desirable to determine the molarity of the solution, the solution shall be standardized and the determined molarity used in subsequent calculations. The standardization procedure shall be as follows:

7.4.1.1 To standardize, place 50 mL of glacial acetic acid and 1 mL of concentrated hydrochloric acid (Warning—See Note 4 in a 500-mL iodine number flask. Chill the solution in a bath for approximately 10 min and, with constant swirling of the flask, add from a 10-mL calibrated buret,  $5 \pm 0.01$  mL of the bromide-bromate standard solution at the rate of 1 or 2 drops per second. Stopper the flask immediately, shake the contents, place it again in the ice bath, and add 5 mL of KI solution in the lip of the flask. After 5 min remove the flask from the ice bath and allow the KI solution to flow into the flask by slowly removing the stopper. Shake vigorously, add 100 mL of water in such a manner as to rinse the stopper, lip and walls of the flask, and titrate promptly with sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) solution. Near the end of the titration, add 1 mL of starch indicator solution and titrate slowly to disappearance of the blue color. Calculate the molarity of the bromide-bromate solution as follows:

$$M_1 = \frac{AM_2}{(5)(2)} \quad (1)$$

where:

$M_1$  = molarity of the bromide-bromate solution, as Br<sub>2</sub>,  
 $A$  = millilitres of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution required for titration of the bromide-bromate solution, and,  
 $M_2$  = molarity of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution,  
 5 = millilitres of bromide—bromate solution, and  
 2 = number of electrons transferred during redox titration of bromide-bromate solution.

Repeat the standardization until duplicate determinations do not differ from the mean by more than  $\pm 0.002$  M.

NOTE 4—Warning: Poison corrosive. May be fatal if swallowed. Liquid and vapor causes severe burns. Harmful if inhaled; relative density 1.19.

7.5 *Methanol*—(Warning—See Note 5.)

NOTE 5—Warning: Flammable. Vapor harmful. Can be fatal or cause blindness if swallowed or inhaled. Cannot be made non-poisonous.

7.6 *Potassium Iodide Solution (150 g/L)*—Dissolve 150 g of

<sup>7</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory*, BDH Ltd., Poole, Dorset, U.K. and the *United States Pharmacopeia and National Formulary*, U. S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

potassium iodide (KI) in water and dilute to 1 L.

**7.7 Sodium Thiosulfate, Standard Solution (0.1 M)**—Dissolve 25 g of sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) in water and add 0.1 g of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) to stabilize the solution. Dilute to 1 L and mix thoroughly by shaking. Standardize by any accepted procedure that determines the molarity with an error not greater than  $\pm 0.0002$ . Restandardize at intervals frequent enough to detect changes of 0.0005 in molarity.

**7.8 Starch Indication Solution**—Mix 5 g of soluble starch with about 3 to 5 mL of water. If desired, add about 0.65 g salicylic acid as preservative. Add the slurry to 500 mL of boiling water and continue boiling for 5 to 10 min. Allow to cool, and decant the clear, supernatant liquid into glass bottles and seal well. Starch solutions (some preserved with salicylic acid) are also commercially available and may be substituted.

**7.9 Sulfuric Acid (1 + 5)**—Carefully mix one volume of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ , rel dens 1.84) with five volumes of water.

**NOTE 6—Warning:** Poison. Corrosive. Strong oxidizer. Contact with organic material can cause fire. Can be fatal if swallowed.

**7.10 Titration Solvent**—Prepare 1 L of titration solvent by mixing the following volumes of materials: 714 mL of glacial acetic acid, 134 mL of 1,1,1-trichloroethane (or dichloromethane), 134 mL of methanol, and 18 mL of  $\text{H}_2\text{SO}_4$  (1 + 5).

**7.11 1,1,1-Trichloroethane**—(Warning—See Note 7.)

**NOTE 7—Warning:** Harmful if inhaled. High concentrations can cause unconsciousness or death. Contact may cause skin irritation and dermatitis.

**7.12 Dichloromethane**—(Warning—See Note 8.)

**NOTE 8**—The replacement of 1,1,1-trichloroethane, an ozone-depleting chemical, is necessary because its manufacture and import has been discontinued. Dichloromethane is temporarily being allowed as an alternative to 1,1,1-trichloroethane until a permanent replacement can be identified and adopted by ASTM. A program to identify and evaluate candidate solvents is currently underway in Subcommittee D02.04.

**NOTE 9**—The user of this test method may choose to use either 1,1,1-trichloroethane or dichloromethane to the exclusion of the other solvent. The selected solvent is to be used for all operations, that is, in the preparation of the titration solvent, for the dilution of samples, and as the titration blank.

## 8. Check Procedure

**8.1** In case of doubt in applying the procedure to actual samples, the reagents and techniques can be checked by means of determinations on freshly purified cyclohexene or diisobutene. (Warning—See Note 9.) Proceed in accordance with Section 9, using a sample of either 0.6 to 1 g freshly purified cyclohexene or diisobutene (see Table 1) or 6 to 10 g of 10 mass percent solutions of these materials in 1,1,1-trichloroethane.

TABLE 1 Physical Properties of Purified Olefins

Compound	Boiling Point, °C	Density at 20°C, g/mL	Index of Refraction, $D_{\text{Line}}$ at 20°C
Cyclohexene	82.5 to 83.5	0.8100	1.4465
Diisobutene <sup>a</sup>	101 to 102.5	0.7175 $\pm 0.0015$	1.4112

<sup>a</sup> Only the 2,4,4-trimethyl-1-pentene isomer.

**NOTE 10—Warning:** Flammable.

**8.2** If the reagents and techniques are correct, values within the following should be obtained:

Standard	Bromine Number
Cyclohexene, purified (see 7.4.1, 9.3, and Note 11) Note 10)	187 to 199 (see 9.5)
Cyclohexene, 10 % solution	18 to 20
Diisobutene, purified (see 7.4.1, 8.3, and Note 11) Note 10)	136 to 144 (see 9.5)
Diisobutene, 10 % solution	13 to 15

The reference olefins yielding the above results are characterized by the properties shown in Table 1. The theoretical bromine numbers of cyclohexene and diisobutene are 194.6 and 142.4, respectively.

**8.3** Purified samples of cyclohexene and diisobutene can be prepared from cyclohexene and diisobutene,<sup>8</sup> by the following procedure:

**8.3.1** Add 65 g of activated silica gel, 75 to 150  $\mu\text{m}$  (100 to 200 mesh) manufactured to ensure minimum olefin polymerization<sup>9</sup> to a column approximately 16 mm in inside diameter and 760 mm in length, that has been tapered at the lower end and that contains a small plug of glass wool at the bottom. A 100-mL buret, or any column that will give a height-to-diameter ratio of the silica gel of at least 30:1, will be suitable. Tap the column during the adding of the gel to permit uniform packing.

**8.3.2** To the column add 30 mL of the olefin to be purified. When the olefin disappears into the gel, fill the column with methanol. Discard the first 10 mL of percolate and collect the next 10 mL that is the purified olefin for test of the bromine number procedure. Determine and record the density and refractive index of the purified samples at 20°C. Discard the remaining percolate.

**NOTE 11—Caution:** If distillation of impure olefins is needed as a pre-purification step, a few pellets of potassium hydroxide should be placed in the distillation flask and at least 10 % residue should remain to minimize the hazards from decomposition of any peroxides that may be present.

## 9. Procedure

**9.1** Place 10 mL of 1,1,1-trichloroethane or dichloromethane in a 50-mL volumetric flask and, by means of a pipet, introduce a test specimen as indicated in Table 2. Either obtain the weight of specimen introduced by difference between the weight (to the nearest 1 mg) of the flask before and

TABLE 2 Specimen Size

Bromine Number	Specimen Size, g
0 to 10	20 to 16
Over 10 to 20	10 to 8
Over 20 to 50	5 to 4
Over 50 to 100	2 to 1.5
Over 100 to 150	1.0 to 0.8
Over 150 to 200	0.8 to 0.6

<sup>8</sup> Available from Eastman, Rochester, NY, by specifying No. 13019 (cyclohexene) and No. P2125 (diisobutene).

<sup>9</sup> Available from W.R. Grace and Company, Davison Chemical Division, Baltimore, MD 21203, by specifying Code 923.

after addition of specimen or, if the density is known accurately, calculate the weight from the measured volume. Fill the flask to the mark with the selected solvent and mix well. (Warning—See Note 12.)

NOTE 12—Warning: Hydrocarbons, particularly those boiling below 205°C (400°F), are flammable.

9.1.1 Frequently, the order of magnitude of the bromine number of a specimen is unknown. In this case, a trial test is recommended using a 2-g specimen in order to obtain the approximate magnitude of the bromine number. This exploratory test shall be followed with another determination using the appropriate specimen size as indicated in Table 2.

9.1.2 The test specimen taken shall not exceed 10 mL and the volume of bromide-bromate titrant used shall not exceed 10 mL and no separation of the reaction mixture into two phases shall occur during the titration. Difficulty may be experienced in dissolving specimen of the high boiling ranges in the titration solvent; this can be prevented by the addition of a small quantity of toluene.

9.2 Cool the titration vessel to 0 to 5°C (32 to 41°F) and maintain the contents at this temperature throughout the titration. Switch on the titrimer, and allow the electrical circuit to become stabilized.

9.3 Introduce 110 mL of titration solvent into the vessel and pipet in a 5-mL aliquot of the sample solution from the 50-mL volumetric flask. Switch on the stirrer and adjust to a rapid stirring rate, but avoid any tendency for air bubbles to be drawn down to the solution.

9.4 Set the end point potential. With each instrument, the manufacturer's instructions should be followed for end point setting and to achieve the sensitivity in the platinum electrode circuit specified in 6.1.

9.5 Depending on the titrator apparatus, add the bromide-bromate solution manually or by microprocessor control in small increments from the buret. The endpoint of the titration is achieved when the potential reaches the pre-set value (see 9.4) and persists for more than 30 s.

9.6 *Blanks*—Perform duplicate blank titrations of each batch of titration solvent. Do this by repeating 9.3 through 9.5 for each blank determination, substituting 5 mL of the selected solvent (1,1,1-trichloroethane or dichloromethane) in place of the sample solution. Less than 0.1 mL of bromide-bromate solution should be required. If more than 0.1 mL is used, discard the analysis, prepare fresh titration solvent and fresh reagents and repeat the analysis.

## 10. Calculation

10.1 Calculate the bromine number as follows:

$$\text{bromine number} = \frac{(A - B)(M_1)(15.98)}{W} \quad (2)$$

where:

- $A$  = millilitres of bromide-bromate solution required for titration of the test aliquot,  
 $B$  = millilitres of bromide-bromate solution required for titration of the blank,

- $M_1$  = molarity of the bromide-bromate solution, as  $\text{Br}_2$ ,  
 $W$  = grams of test specimen in the aliquot, and  
 15.98 = factor for converting g of bromine per 100 g of specimen and incorporating molecular weight of bromine (as  $\text{Br}_2$ ) and conversion of mL to L.

## 11. Precision and Bias <sup>10</sup>

11.1 *Precision*—The precision of this test method as determined by the statistical examination of interlaboratory test results is as follows:

11.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty.

Petroleum distillates:

$$90\% \text{ distillation point under } 205^\circ\text{C } r = 0.11 (X^{0.70}) \quad (3)$$

$$90\% \text{ distillation point between } 205 \text{ and } 327^\circ\text{C } r = 0.11 (X^{0.67}) \quad (4)$$

where:  $X$  = sample mean.

Commercial olefins:

$$r = 3 \quad (5)$$

11.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, exceed the following values only in one case in twenty:

Petroleum Distillates:

$$90\% \text{ distillation point under } 205^\circ\text{C } R = 0.72 (X^{0.70}) \quad (6)$$

$$90\% \text{ distillation point between } 205 \text{ and } 327^\circ\text{C } R = 0.78 (X^{0.67}) \quad (7)$$

where:  $X$  = sample mean.

Commercial olefins <sup>11</sup>

$$R = 12 \quad (8)$$

11.2 *Bias*—The procedure for measuring bromine number has no bias because the value of bromine number can be defined only in terms of a test method.

NOTE 13—The precision of this test method was determined using 1,1,1-trichloroethane as the sample dilution solvent and as a component of the titration solvent. It is not known whether the precision estimates are applicable when using dichloromethane in place of 1,1,1-trichloroethane.

## 12. Keywords

12.1 aliphatic olefins; bromine number; electrometric titration; petroleum distillates

<sup>10</sup> Refer to ASTM Research Report RR: D02-1290 covering the round robin data and statistical analysis for products having 90 % distillation points under 205°C.

<sup>11</sup> Provisional value obtained from a limited amount of data.

## ANNEXES

### (Mandatory Information)

#### A1. REPORTED BEHAVIOR OF COMPOUNDS BY THE ELECTROMETRIC BROMINE NUMBER METHOD

A1.1 Technically, the bromine number is the number of grams of bromine reacting with 100 g of the sample under prescribed conditions. By this definition, bromine consumed by addition, substitution, oxidation, and reactions with sulfur, nitrogen, and oxygen-containing compounds is included in the bromine number of the material. The use of the bromine number under determination in the estimation of olefinic unsaturation depends on the fact that the addition reaction proceeds rapidly and completely under most conditions. The addition of bromine proceeds readily at temperatures down to or below 0°C. Decreasing temperature of reaction, time of contact, and concentration of free bromine tend to retard both substitution and oxidation reactions. Other factors, such as solvent medium, extent of agitation, and exposure to actinic light, also influence the rate of the various reactions.

A1.2 Experience has shown that no single set of test conditions will direct the reaction of bromine in one manner to the exclusion of the others. For this reason, the conditions of bromine number tests are usually established on an empirical basis to give reasonable values with representative materials.

A1.3 The possibility of multiple reactions occurring concurrently and the variable behavior to certain materials in the presence of bromine imposes an element of uncertainty in the interpretation of results. A knowledge of the material being handled and its response to bromine greatly reduces the risk of misinterpretation.

A1.4 Bromine number data have been obtained for a variety of petroleum hydrocarbons and certain nonhydrocarbons associated with petroleum, by the electrometer bromine number procedure. These data, which were submitted by cooperators, are presented in Table A1.1.

A1.5 It is intended that this information serve as a general guide in the interpretation of bromine numbers on petroleum products. It is recognized that the bromine number data recorded in this table are of limited value owing to incompleteness; however, it is considered that their usefulness will be amplified as more bromine number data are contributed by cooperators.

**TABLE A1.1 Reported Behavior of Compounds by the Electrometric Bromine Number Method**

Compound	Purity, % <sup>A</sup>	Bromine Number		
		Theory	Found	Deviation
Paraffins				
Hexane	99.96 <sup>B</sup>	0.0	0.0	0.0
2-Methylhexane	99.88	0.0	0.0	0.1
Heptane	<sup>C</sup>	0.0	0.1	+ 0.1
Octane	99.94	0.0	0.0	0.0
2,2,4-Trimethylpentane	99.96	0.0	0.1	+ 0.1
Straight Chain Olefins				
1-Pentene	99.7	228.0	208	-20
<i>trans</i> -2-Pentene	99.91	228.0	235	+ 7
1-Hexene	99.80	189.9	181	-9
<i>cis</i> -2-Hexene	99.83	189.9	189	-1
<i>trans</i> -2-Hexene	99.87	189.9	189	-1
<i>cis</i> -3-Hexene	99.94	189.9	193	+ 3
<i>trans</i> -3-Hexene	...	189.9	191.4	+ 1.5
1-Heptene	99.8	162.8	136	-27
<i>trans</i> -2-Heptene	99.85	162.8	163	0
<i>trans</i> -3-Heptene	99.80	162.8	163	0
1-Octene	99.7	142.4	132	-10
2-Octene	...	142.4	139	- 3
<i>trans</i> -4-Octene	99.84	142.4	149	+ 7
1-Decene	99.89	114.1	111.4	- 2.7
1-Dodecene	99.9	95.1	82.9	- 12.2
1-Tridecene	99.8	87.7	81.4	-6.3
1-Tetradecene	99.7	81.4	70.8	- 10.6
1-Pentadecene	99.8	76.0	62.9	- 13.1
1-Hexadecene	99.84	71.2	62.8	- 8.4
Branched Chain Olefins				
2-Methyl-1-butene	99.90	228.0	231.8	+ 3.8
2-Methyl-2-butene	99.94	228.0	235	7
2,3-Dimethyl-1-butene	99.86	189.9	194	+ 4
3,3-Dimethyl-1-butene	99.91	189.9	167	- 23

TABLE A1.1 *Continued*

Compound	Purity, % <sup>A</sup>	Bromine Number		
		Theory	Found	Deviation
2-Ethyl-1-butene	99.90	189.9	198	+ 8
2,3-Dimethyl-2-butene	99.90	189.9	191	+ 1
2-Methyl-1-pentene	99.92	189.9	182	- 8
3-Methyl-1-pentene	99.70	189.9	152	- 38
4-Methyl-1-pentene	99.82	189.9	176	- 14
2-Methyl-2-pentene	99.91	189.9	190	0
3-Methyl- <i>cis</i> -2-pentene	99.85	189.9	193.7	+ 3.8
3-Methyl- <i>trans</i> -2-pentene	99.86	189.9	191	+ 1
4-Methyl- <i>cis</i> -2-pentene	99.92	189.9	190	0
4-Methyl- <i>trans</i> -2-pentene	99.75	189.9	190	0
2,3,3-Trimethyl-1-butene	99.94	162.8	161	- 2
3-Methyl-2-Ethyl-1-butene	99.8	162.8	165.4	+ 2.6
2,3-Dimethyl-1-pentene	99.80	162.8	158.5	- 4.3
2,4-Dimethyl-1-pentene	99.87	162.8	152.8	- 10.0
2,3-Dimethyl-2-pentene	99.6	162.8	162.3	- 0.5
4,4-Dimethyl- <i>cis</i> -2-pentene	99.79	162.8	159	- 4
4,4-Dimethyl- <i>trans</i> -2-pentene	99.91	162.8	158	- 5
3-Ethyl-1-pentene	99.85	162.8	173.1	+ 10.3
3-Ethyl-2-pentene	99.80	162.8	165	+ 2
2-Methyl-1-hexene	99.88	162.8	161	- 2
5-Methyl-1-hexene	99.80	162.8	154	- 9
3-Methyl- <i>cis</i> -2-hexene	99.8	162.8	163.6	+ 0.8
2-Methyl- <i>trans</i> -3-hexene	99.9	162.8	163.4	+ 0.6
2-Methyl-3-Ethyl-1-pentene	99.81	142.4	139.8	- 2.6
2,4,4-Trimethyl-1-pentene	99.91	142.4	137.0	- 5.4
2,4,4-Trimethyl-2-pentene	99.92	142.4	141.2	- 1.2
Diisobutene	<i>D</i>	142.4	139.8 <sup>D</sup>	- 2.6
2-Ethyl-1-hexene	<i>E</i>	142.4	140.2	- 2.2
2,3-Dimethyl-2-hexene	99.71	142.4	143	+ 1
2,5-Dimethyl-2-hexene	99.8	142.4	142.8	+ 0.4
2,2-Dimethyl- <i>trans</i> -3-hexene	99.80	142.4	139	- 3
Triisobutene	99.0 <sup>F</sup>	95	57.5	- 37.5
Nonconjugated Cyclic Diolefins				
4-Ethenyl-1-cyclohexene (4-vinyl-1-cyclohexene)	99.90	295.5	210 <sup>G</sup>	(- 85)
di-1,8(9)- <i>p</i> -Menthadiene (dipentene)	98-100 <sup>H</sup>	234.6	225.2	- 9.4
Conjugated Diolefins				
2-Methyl-1,3-butadiene (isoprene)	99.96	470	235.7	- 234
<i>cis</i> -1,3-Pentadiene	99.92	470	285.3	- 185
<i>trans</i> -1,3-Pentadiene	99.92	470	234	- 236
2-Methyl-1,3-Pentadiene	95 + <sup>I</sup>	389	197.3	- 192
2,3-Dimethyl-1,3-Butadiene	99.93	389	186.1	- 203
Nonconjugated Diolefins				
1,2-Pentadiene	99.66	470	230	- 240
1,4-Pentadiene	99.93	470	185	- 285
2,3-Pentadiene	99.85	470	227	- 243
1,5-Hexadiene	99.89	389	352	- 37
Aromatics with Unsaturated Side Chains				
Phenylethylene (styrene)	<i>J</i>	153.4	123.6	- 29.8
Methylphenylethylene ( $\alpha$ -methylstyrene)	<i>J</i>	135.3	133.2	- 2.1
Amylbenzene	97.8 <sup>K</sup>	135.2	0.0	135.2
Cyclic Olefins				
Cyclopentene	99.97	234.6	237	+ 2
Cyclohexene	99.98	194.6	193.2	- 1.4
Cyclohexene	<i>D</i>	194.6	192.8 <sup>D</sup>	- 1.8
1-Methylcyclopentene	99.86	194.6	209	+ 14
1-Methylcyclohexene	99.82	166	162	- 4
Ethenylcyclopentane (Vinylcyclopentane)	99.91	166	164	- 2
Ethylidenecyclopentane	99.96	166.2	167.7	+ 1.5
1,2-Dimethylcyclohexene	99.94	145.0	150.9	+ 5.9
3-Cyclopentyl-1-propene	99.87	145.0	140.9	- 4.1
Ethylidenecyclohexane	99.86	145.0	147.0	+ 2.0
Ethenylcyclohexane (Vinylcyclohexane)	99.95	145	139	- 6
1-Ethylcyclohexene	99.83	145	146.6	+ 1.6
Indene	...	137.7	134	- 4
Aromatics, Monocyclic				
Benzene	99.98	0.0	0.1	+ 0.1
Toluene	99.97	0.0	0.1	+ 0.1

TABLE A1.1 *Continued*

Compound	Purity, % <sup>A</sup>	Bromine Number		
		Theory	Found	Deviation
o-Xylene	99 + <sup>L</sup>	0.0	0.0	0.0
m-Xylene	99 + <sup>L</sup>	0.0	0.0	0.0
p-Xylene	99 + <sup>L</sup>	0.0	0.0	0.0
isopropylbenzene (Cumene)	99.95	0.0	0.0	0.0
1,2,4-Trimethylbenzene (Pseudocumene)	99.67	0.0	0	0
1,3,5-Trimethylbenzene (Mesitylene)	<sup>M</sup>	0.0	0.3	+ 0.3
1,3-Dimethyl-4-ethylbenzene	99.9	0.0	0.0	0.0
1,2,4,5-Tetramethylbenzene (Durene)	99.86	0.0	0.1	+ 0.1
1,2,3,5-Tetramethylbenzene (Isodurene)	<sup>M</sup>	0.0	0.3	+ 0.3
t-Butylbenzene	99.73 <sup>B</sup>	0.0	0.0	0.0
t-Amylbenzene	<sup>F</sup>	0.0	0.7	+ 0.7
Aromatics, Bicyclic				
Phenylbenzene (Biphenyl)	<sup>M</sup>	0.0	0.0	0.0
Naphthalene	99.96	0.0	0	0
1, 2,3,4-Tetrahydronaphthalene (Tetralin)	99.9	0.0	0.2	+ 0.2
1-Methylnaphthalene	99.78	0.0	0.0	0.0
2-Methylnaphthalene	99.91	0.0	0.0	0.0
2,3-Dihydroindene (Indan)	99.9	0.0	0.0	0.0
Cyclohexylbenzene	99.93	0.0	0	0
Aromatics, Polycyclic				
Athracene	<sup>M</sup>	0.0	11.8	+ 11.8
Phenanthrene	<sup>M</sup>	0.0	3.9	+ 3.9
Cycloparaffins				
Methylcyclopentane	99.99 <sup>B</sup>	0.0	0.0	0.0
Methylcyclohexane	99.97	0.0	0	0
Isopropylcyclopentane	99.8	0.0	0.0	0.0
cis-Hexahydroindan (cis-Hydrindan)	99.94	0.0	0.0	0.0
trans-Hexahydroindan (trans-Hydrindan)	99.71	0.0	0.0	0.0
tert-Butylcyclohexane	99.95	0.0	0	0
Cyclopentylcyclopentane	99.95	0.0	0.0	0.0
cis-Decahydronaphthalene (cis-decalin)	98 + <sup>I</sup>	0.0	0.11	+ 0.11
trans-Decahydronaphthalene (trans-decalin)	98 + <sup>I</sup>	0.0	1.64	+ 1.64
Sulfur Compounds				
Ethanethiol (ethyl mercaptan)	99.95	0.0	209	+ 209
3-Thiapentane (ethyl sulfide)	99.94	0.0	184	+ 184
2,3-Dithiabutane (methylsulfide)	99.97	0.0	1.1	+ 1.1
Thiacyclobutane (trimethylene sulfide)	99.95	0.0	214	+ 214
Thophene	99.99	0.0	0.4	+ 0.4
Thiacyclopentane (tetrahydrothiophene)	99.95	0.0	183	+ 183
3,4-Dithiahexane (diethylsulfide)	99.90	0.0	0.4	+ 0.4
2-Methyl 2-propanethiol (tert-butyl mercaptan)	99.92	0.0	141	+ 141
1-Pentanethiol (amyl mercaptan)	99.92	0.0	83	+ 83
Nitrogen Compounds				
Bromine	99.85	0.0	11.8	+ 11.8
iodine	<sup>N</sup>	0.0	1.4	+ 1.4
2-Methylpyridine	99.90	0.0	0.9	+ 0.9
4-Methylpyridine	99 + <sup>O</sup>	0.0	1.7	+ 1.7
2,4,6-Trimethylpyridine	99 + <sup>O</sup>	0.0	2.7	+ 2.7
2-(5-nonyl) pyridine	<sup>M</sup>	0.0	1.4	+ 1.4
Pyrrole	99.99	0.0	873	+ 873
2-Methylpyrrole	98 + <sup>N</sup>	0.0	708	+ 708
2,4-Dimethylpyrrole	98 + <sup>N</sup>	0.0	484	+ 484
2,5-Dimethylpyrrole	99.9 <sup>P</sup>	0.0	869	+ 869
2,4-Dimethyl-3-ethylpyrrole	98 + <sup>N</sup>	0.0	248	+ 248
1-Butyl 1-(1) pyrrole	98 + <sup>N</sup>	0.0	472	+ 472
Oxygen Compounds				
Acetone	<sup>O</sup>	0.0	0.0	0.0
Methyl ethyl ketone	<sup>R</sup>	0.0	0.0	0.0



TABLE A1.1 *Continued*

Compound	Purity, % <sup>A</sup>	Bromine Number		
		Theory	Found	Deviation
Miscellaneous				
Ethanolamine	M	0.0	1.5	+ 5
Ethylene dichloride	O	0.0	0.0	0.0
Ethylene dibromide	O	0.0	0.0	0.0
Tetraethyllead (TEL)	S	(49.5) <sup>T</sup>	52.7	(+ 3.2)
Tetramethyllead (TML)	S	(59.8) <sup>T</sup>	62.6	(+ 2.8)
AK 33X	S	(73.4) <sup>T</sup>	0.6	(-72.8)
"Ethyl" orange dye	S	...	0.0	...

<sup>A</sup> API Standard Samples, unless otherwise noted.

<sup>B</sup> Phillips research grade product.

<sup>C</sup> Phillips pure grade product, distilled, heart-cut percolated through Si gel.

<sup>D</sup> Average value obtained in September 1957 Cooperative Program on purified Eastman product.

<sup>E</sup> Dow Research Chemical.

<sup>F</sup> Purity not stated.

<sup>G</sup> Approximate value.

<sup>H</sup> Hercules Inc., experimental sample.

<sup>I</sup> From Penn State University.

<sup>J</sup> Eastman white label product, distilled, 50-mm pressure just prior to test.

<sup>K</sup> M C and B chemical. Purity determined by GC, impurities not identified.

<sup>L</sup> Phillips pure grade product.

<sup>M</sup> Eastman white label product.

<sup>N</sup> Samples supplied by API Project 52.

<sup>O</sup> Purity estimated by spectra and GLC.

<sup>P</sup> Purity estimated from freezing point.

<sup>Q</sup> B and A Reagent chemical (Code No. 1004).

<sup>R</sup> M C and B chemical (Code No. 2609).

<sup>S</sup> Ethyl Corporation products.

<sup>T</sup> Calculated values based on the reaction of one mole of bromine with the organometallic compound.

## A2. CALCULATION OF OLEFIN CONTENT

### A2.1 Scope

A2.1.1 This procedure covers the calculation of the volume percentage of olefins from the bromine number in straight-run, reformed, cracked gasolines and commercial gasolines that have a 90 % boiling point below 200°C (392°F); and turbine fuel and kerosine etc., boiling below 315°C (600°F) and having a bromine number of less than 20.

A2.1.2 The procedure is not intended for synthetic olefinic blends of pure or nearly pure compounds having a boiling range of less than 14°C (25°F).

A2.1.3 Sulfur, nitrogen, or oxygen compounds, if present in concentrations of 1 volume % or greater will reduce the accuracy (see Note A2.1).

### A2.2 Procedure

A2.2.1 Determine the bromine number in accordance with this test method.

NOTE A2.1—For information on types of compounds that may yield anomalous data in the bromine number test, see Annex A1. In the case of special samples that contain high concentrations of certain hydrocarbon types, caution in the interpretation of the bromine number is needed.

A2.2.2 Calculate the concentration of olefins from the bromine number as follows :

$$\text{olefins, mass \%} = f BM/160 \quad (\text{A2.1})$$

where:

$f$  = boiling range correction (see Fig. A2.1 and Table A2.1),

$B$  = bromine number expressed as grams of bromine/100 g of sample, and

$M$  = molecular weight (relative molecular mass) of olefins (see Table A2.2).

NOTE A2.2—The boiling range correction is needed for cracked naphthas since it is an empirical fact that the percentage by volume of olefins is higher in the lower boiling fractions and that these olefins are also of lower relative molecular mass (molecular weight).

A2.2.3 Using the 50 % boiling point (see Test Method D 86), estimate the average density of the olefins using Fig. A2.2. Multiply the mass percentage of olefins (as calculated in A2.2.2) by the ratio of the density of the original sample to the density of the olefins to obtain percentage by volume as follows:

$$\text{olefins, volume \%} = (A/B) \times C \quad (\text{A2.2})$$

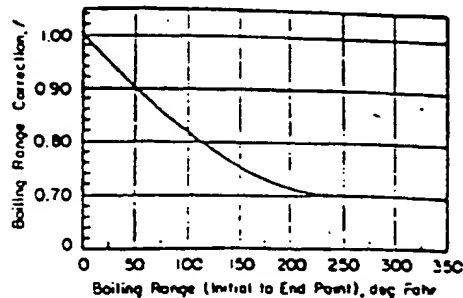


FIG. A2.1 Boiling Range Correction

TABLE A2.1 Boiling Range Corrections for Olefins

Boiling Range Correction, $f$	Boiling Range, °C (°F) Initial to End, (see Test Method D 86)
1.00	0 (0)
0.975	7 (13)
0.950	14 (25)
0.925	21 (38)
0.900	28 (50)
0.875	38 (68)
0.850	43 (78)
0.825	53 (95)
0.800	62 (112)
0.775	72 (130)
0.750	95 (152)
0.725	99 (178)
0.700	125 or greater (>25)

TABLE A2.2 Relation of Average Relative Molecular Mass (Molecular Weight) to 50 % Boiling Point by Test Method D 86

50 % Boiling Point, °C (°F)	Average Molecular Weight of Olefins
38 (100)	72
66 (150)	83
93 (200)	96
121 (250)	110
149 (300)	127
177 (350)	145
204 (400)	164
232 (450)	186

where:

- $A$  = density of the sample,  
 $B$  = average density of the olefins, and  
 $C$  = mass percentage of olefins.

## A2.3 Precision<sup>12</sup>

A2.3.1 The precision of this test method as obtained by statistical examination of interlaboratory test results is as follows:

<sup>12</sup> The results of cooperative data were last published in the 1996 Annual Book of ASTM Standards, Part 17, and are filed at ASTM Headquarters as Research Report No. RR36:D-2.

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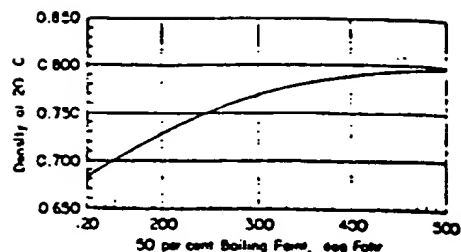


FIG. A2.2 Relation of Density to the 50 % Boiling Point

A2.3.1.1 *Repeatability*— The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Straight-Run Fuels (less than 1 volume % olefins)	Cracked Gasolines (1 to 25 volume % olefins)
0.2	0.6

A2.3.1.2 *Reproducibility*— The difference between two single and independent results, obtained by different operators, working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Straight-Run Fuels (less than 1 volume % olefins)	Cracked Gasolines (1 to 25 volume % olefins)
0.4	3

A2.3.2 *Bias*—The procedure for calculating olefin content has no bias because the value obtained can be defined only in terms of a procedure.

NOTE A2.3—The precision for this test method was not obtained in accordance with RR: D02-1007.



## Standard Test Method for Bromine Index of Petroleum Hydrocarbons by Electrometric Titration<sup>1</sup>

This standard is issued under the fixed designation D 2710; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This test method covers the determination of the amount of bromine-reactive material in petroleum hydrocarbons and is thus a measure of trace amounts of unsaturates in these materials. It is applicable to materials having bromine indexes below 1000.

1.2 This test method is applicable only to essentially olefin-free hydrocarbons or mixtures that are substantially free from material lighter than isobutane and have a distillation end point under 288°C (550°F).

1.3 The values stated in SI units are to be regarded as standard. The values stated in inch-pound units are for information only.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Sections 7 and 8.

NOTE 1—This procedure has been cooperatively tested on materials with bromine indexes in the range from 100 to 1000. These materials include petroleum distillates such as straight-run and hydrocracked naphtha, reformer feed, kerosine, and aviation turbine fuel.

NOTE 2—Materials with bromine index greater than 1000 should be tested for bromine number using Test Method D 1159/IP 130.

NOTE 3—Bromine index of industrial aromatic hydrocarbons should be determined using Test Method D 1492 or D 5776.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 1159 Test Method for Bromine Number of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration<sup>2</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.OD on Physical Methods.

Current edition approved June 10, 1999. Published August 1999. Originally published as D 2710 – 68. Last previous edition D 2710 – 94.

In the IP, this test method is under the jurisdiction of the Standardization Committee.

<sup>2</sup> *Annual Book of ASTM Standards*, Vol 05.01.

D 1492 Test Method for Bromine Index of Aromatic Hydrocarbons by Coulometric Titration<sup>3</sup>

D 5776 Test Method for Bromine Index of Aromatic Hydrocarbons by Electrometric Titration<sup>3</sup>

### 3. Terminology

#### 3.1 Definition:

3.1.1 *bromine index*—the number of milligrams of bromine that will react with 100 g of sample under the conditions of the test.

### 4. Summary of Test Method

4.1 A known mass of the sample dissolved in a specified solvent is titrated with standard bromide-bromate solution. The end point is indicated by a dead stop electrometric titration apparatus when the presence of free bromine causes a sudden change in the electrical conductivity of the system.

### 5. Significance and Use

5.1 This test method provides a measure of trace amounts of unsaturated hydrocarbons in petroleum distillates boiling up to 288°C (550°F). An estimate of the quantity of these materials is useful in assessing the suitability of the lighter fractions for use as reaction solvents.

### 6. Apparatus

6.1 *Electrometric End Point Titration Apparatus*—Any apparatus designed to perform titrations to pre-set end points (see Note 4) may be used in conjunction with a high-resistance polarizing current supply capable of maintaining approximately 0.8 V across two platinum electrodes and with a sensitivity such that a voltage change of approximately 50 mV at these electrodes is sufficient to indicate the end point. Other types of commercially available electric titrimeters, including certain pH meters, have also been found to be suitable.

NOTE 4—Pre-set end point indicated with polarized electrodes provides a detection technique similar to the dead stop technique specified in previous versions of this test method.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 06.04.

**6.2 Titration Vessel**—A jacketed glass vessel of approximately 150-mL capacity of such a form that can be conveniently maintained at 0 to 5°C (32 to 41°F). A pair of platinum electrodes spaced not more than 5 mm apart shall be mounted to extend well below the liquid level. Stirring shall be by a mechanical or electromagnetic stirrer and shall be rapid, but not so vigorous as to draw air bubbles down to the electrodes.

**6.3 Burets**, 10 and 50-mL capacity.

**6.4 Iodine Number Flasks**, glass-stoppered, 500-mL capacity.

## 7. Reagents

**7.1 Purity of Reagents**—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the American Chemical Society where such specifications are available.<sup>4</sup> Other grades may be used, providing it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

**7.2 Purity of Water**—Unless otherwise indicated, references to water shall be understood to mean distilled water, or water of equivalent purity.

### 7.3 Preparation and Standardization:

**7.3.1 Bromide-Bromate Standard Solution (0.05 N)**—Dissolve 5.1 g of potassium bromide (KBr) and 1.4 g potassium bromate (KBrO<sub>3</sub>) in water and dilute to 1 L. Standardize to four significant figures as follows: Place 50 mL of glacial acetic acid (**Warning**—See Note 5.) and 1 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) (**Warning**—See Note 6.) in a 500-mL iodine number flask. Chill the solution in an ice bath for approximately 10 min, and with constant swirling of the flask, add from a 50-mL buret 40 to 45 mL of bromide-bromate solution, estimated to the nearest 0.01 mL, at a rate such that the addition takes between 90 and 120 s. Stopper the flask immediately, shake the contents, place it again in the ice bath, and add 5 mL of potassium iodide (KI) solution in the lip of the flask. After 5 min remove the flask from the ice bath and allow the KI solution to flow into the flask by slowly removing the stopper. Shake vigorously, add 100 mL of water in such a manner as to rinse the stopper, lip, and walls of the flask, and titrate promptly with the standard sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) solution. Near the end of the titration, add 1 mL of starch indicator solution and titrate slowly to the disappearance of the blue color. Calculate the normality of the bromide-bromate solution as follows:

$$N_1 = A_2 N_2 / A_1 \quad (1)$$

where:

$N_1$  = normality of the bromide-bromate solution,  
 $A_1$  = millilitres of the bromide-bromate solution,  
 $N_2$  = normality of the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution, and

$A_2$  = millilitres of the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution required for titration of the bromide-bromate solution.

**NOTE 5**—**Warning:** Poison. Combustible. May be fatal if swallowed. Causes severe burns. Harmful if inhaled.

**NOTE 6**—**Warning:** Poison. Corrosive. May be fatal if swallowed. Liquid and vapor cause severe burns. Harmful if inhaled.

**7.3.2 Potassium Iodide Solution (150 g/L)**—Dissolve 150 g of KI in water and dilute to 1 L.

**7.3.3 Sodium Thiosulfate, Standard Solution (0.05 N)**—Dissolve 12.5 g of sodium thiosulfate pentahydrate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> · 5H<sub>2</sub>O) in water and add 0.01 g of sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) to stabilize the solution. Dilute to 1 L and mix thoroughly by shaking. Standardize by any accepted procedure that determines the normality with an error not greater than ±0.0002. Restandardize at intervals frequent enough to detect changes of 0.0005 in normality.

**7.3.4 Starch Indicator Solution**—Mix 5 g of soluble starch with approximately 3 to 5 mL of water. If desired, add about 0.65 g salicylic acid as preservative. Add the slurry to 500 mL of boiling water and continue boiling for 5 to 10 min. Allow to cool and decant the supernatant liquid into glass bottles and seal well. Starch solutions (some preserved with salicylic acid) are also commercially available and may be substituted.

**7.3.5 Sulfuric Acid (1+5)**—Carefully add 1 volume of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, sp gr 1.84) to 5 volumes of water and thoroughly mix. (**Warning**—See Note 7.)

**NOTE 7**—**Warning:** Poison. Corrosive. Strong Oxidizer. Contact with organic material may cause fire. May be fatal if swallowed.

**7.3.6 Titration Solvent**—Prepare 1 L of titration solvent by mixing the following volumes of materials: 714 mL of glacial acetic acid, 134 mL of 1,1,1-trichloroethane or dichloromethane, 134 mL of methanol, and 18 mL of H<sub>2</sub>SO<sub>4</sub> (1+5) (see 7.3.5).

### 7.4 Solvents:

**7.4.1 Acetic Acid**, glacial. (**Warning**—See Note 5.)

**7.4.2 Methanol** (**Warning**—See Note 8.)

**NOTE 8**—**Warning:** Flammable. Vapor harmful. May be fatal if swallowed. Causes severe burns. Harmful if inhaled.

**7.4.3 1,1,1-Trichloroethane** (**Warning**—See Note 9.)

**7.4.4 Dichloromethane** (**Warning**—See Note 9.)

**NOTE 9**—**Warning:** Harmful if inhaled. High concentrations may cause unconsciousness or death. Contact may cause skin irritation and dermatitis.

**NOTE 10**—The replacement of 1,1,1-trichloroethane, an ozone-depleting chemical, is necessary because its manufacture and import has been discontinued. Dichloromethane is temporarily being allowed as an alternative to 1,1,1-trichloroethane until a permanent replacement can be identified and adopted by ASTM.

**NOTE 11**—The user of this test method may choose to use either 1,1,1-trichloroethane or dichloromethane to the exclusion of the other solvent. The selected solvent is to be used for all operations, including the preparation of the titration solvent and the dilution of samples, if applicable.

**NOTE 12**—Commercially available reagents can be used in place of laboratory preparations.

## 8. Procedure

**8.1** Switch on the titrimeter and allow the electrical circuits to stabilize in accordance with the manufacturer's instructions.

<sup>4</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.2 Cool the titration vessel to 0 to 5°C (32 to 41°F) by circulating a suitable coolant through the jacketed titration vessel.

8.3 Introduce 110 mL of titration solvent into the titration vessel and pipet in a quantity of sample as indicated in Table 1. Switch on the stirrer and adjust to a rapid stirring rate, but avoid any tendency for air bubbles to be drawn down into the solution. Allow the contents to cool to 0 to 5°C (32 to 41°F) and maintain at this temperature throughout the titration. (Warning—See Note 12.)

8.3.1 Frequently the order of magnitude of the bromine index of a sample is unknown. In this case, a trial test is recommended using an 8 to 10-g sample in order to obtain the approximate magnitude of the bromine index. This exploratory test should be followed with another determination using the appropriate sample size as indicated in Table 1.

8.3.2 The sample mass can be determined by obtaining the density of the sample and calculating the mass of a measured volume.

NOTE 13—Warning: Hydrocarbon samples, particularly those boiling below 205°C (400°F), are flammable.

8.4 Set the end point potential. With each instrument, the manufacturer's instructions should be followed for end point setting and to achieve the sensitivity in the platinum electrode circuit specified in 6.1.

8.5 Depending on the titrator apparatus, add the bromide-bromate solution manually or by microprocessor control in small increments from the buret. The end point of the titration is achieved when the potential reaches the pre-set value (see 8.4) and persists for more than 30 s.

8.6 Blanks—Make duplicate blank titrations on each batch of titration solvent and reagents. Less than 0.10 mL of bromide-bromate solution should be required.

## 9. Calculation

9.1 Calculate the bromine index as follows:

$$\text{Bromine index} = [(A - B)N \times 7990]/W \quad (2)$$

TABLE 1 Sample Size

Bromine Index	Sample Size, g
100 to 500	10 to 8
Over 500 to 1000	8 to 4

where:

- A = millilitres of bromide-bromate solution required for titration of the sample,
- B = millilitres of bromide-bromate solution required for titration of the blank,
- N = normality of bromide-bromate solution, and
- W = grams of sample.

## 10. Precision and Bias

### 10.1 Precision:

10.1.1 The precision of this test method as obtained by statistical examination of interlaboratory test results is as follows:

10.1.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed 14 in only one case in twenty.

10.1.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators, working in different laboratories on identical test material, would in the long run, in the normal and correct operation of the test method, exceed 118 in only one case in twenty.

### 10.2 Bias:

10.2.1 The procedure in this test method has no bias because the value of bromine index can be defined only in terms of a test method.

NOTE 14—The precision for this test method was not obtained in accordance with RR:D02-1007.<sup>5</sup>

NOTE 15—It is not known whether the precision estimates are applicable when using dichloromethane as a constituent of the titration solvent.

## 11. Keywords

11.1 bromide-bromate solution; bromine index; electrometric titration; hydrocarbons; petroleum

<sup>5</sup> Annual Book of ASTM Standards, Vol 05.03.

# ANNEX

## (Mandatory Information)

### A1. RESULTS OF BROMINE INDEX COOPERATIVE PROGRAM

A1.1 See Table A1.1 for the bromine index results.

**TABLE A1.1 Bromine Index**

Sample		1091	1092	1093	1094	1095	Pooled
Lab. 1	1	1064	116	576	391	447	
	2	1064	120	576	392	447	
	avg	1064	118	576	392	447	447
2	1	1081	115	573 <sup>A</sup>	349	467	
	2	1102	119	604 <sup>A</sup>	368	474	
	avg	1092	117	589	359	471	471
3	1	1097	147	688	409	544	
	2	1114	136	688	397	544	
	avg	1106	142	688	403	544	544
4	1	1120	124	582	397	416	
	2	...	118	...	399	...	
	avg	(1120)	121	(582)	398	(416)	(416)
5	1	1039	116	532	388	389	
	2	1049	116	537	388	373	
	avg	1044	116	535	388	381	381
6	1	1055	113	549	395	360	
	2	1055	115	548	390	366	
	avg	1055	114	549	393	363	363
7	1	1063	113	573	365	443	
	2	1061	113	566	385	450	
	avg	1062	113	570	375	447	447
8	1	1277	142	718	449	620	
	2	1274	141	719	451	621	
	avg	1276 <sup>B</sup>	142	719 <sup>B</sup>	450	621 <sup>B</sup>	621 <sup>B</sup>
$\bar{X}$ , average		1078	123	584	395	438	
Repeatability							
Degrees of freedom		13	15	11	15	13	31
$\sigma_r$ , standard deviation		5.5	2.2	1.8	6.1	3.8	5
$r$ , repeatability		16.8	6.6	5.6	18.6	11.6	14
Reproducibility							
Degrees of freedom		6	7	6	7	6	32
$\sigma_R$ , standard deviation		28.5	12.1	49.5	26.3	60.3	41
$R$ , reproducibility		99	40	171	88	208	118

<sup>A</sup>Excluded from repeatability calculations.

<sup>B</sup>Excluded from reproducibility calculations. Table A1.1

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## Standard Test Method for Oxidation Stability of Steam Turbine Oils by Rotating Pressure Vessel<sup>1</sup>

This standard is issued under the fixed designation D 2272; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the Department of Defense.*

### 1. Scope

1.1 This test method<sup>2</sup> utilizes an oxygen-pressured vessel to evaluate the oxidation stability of new and in-service turbine oils having the same composition (base stock and additives) in the presence of water and a copper catalyst coil at 150°C.

1.2 The values stated in acceptable SI units are to be regarded as the standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. For specific warning, see 6.2, 6.4, 6.5, 6.6, 6.10, 6.11.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:

- B 1 Specification for Hard-Drawn Copper Wire<sup>3</sup>
- D 235 Specification for Mineral Spirits (Petroleum Spirits) (Hydrocarbon Dry Cleaning Solvent)<sup>4</sup>
- D 329 Specification for Acetone<sup>4</sup>
- D 770 Specification for Isopropyl Alcohol<sup>4</sup>
- D 943 Test Method for Oxidation Characteristics of Inhibited Mineral Oils<sup>5</sup>
- D 1193 Specification for Reagent Water<sup>6</sup>
- D 2112 Test Method for Oxidation Stability of Inhibited Mineral Insulating Oil by Rotating Bomb<sup>7</sup>
- D 4057 Practice for Manual Sampling of Petroleum and

#### Petroleum Products<sup>8</sup>

D 4742 Test Method for Oxidation Stability of Gasoline Automotive Engine Oils by Thin-Film Oxygen Uptake (TFOU)<sup>9</sup>

E 1 Specification for ASTM Thermometers<sup>10</sup>

2.2 *British Standard*:<sup>11</sup>

B2 2000 Part 0: Section 0.1,

IP 37C Thermometer

2.3 *Institute of Petroleum Standard*:<sup>12</sup>

IP 229

### 3. Summary of Test Method

3.1 The test oil, water, and copper catalyst coil, contained in a covered glass container, are placed in a vessel equipped with a pressure gage. The vessel is charged with oxygen to a gage pressure of 620 kPa (90 psi, 6.2 bar) (see Note 1), placed in a constant-temperature oil bath set at 150°C, and rotated axially at 100 rpm at an angle of 30° from the horizontal. The number of minutes required to reach a specific drop in gage pressure is the oxidation stability of the test sample.

NOTE 1—100 kPa = 1.00 bar = 14.5 psi.

### 4. Significance and Use

4.1 The estimate of oxidation stability is useful in controlling the continuity of this property for batch acceptance of production lots having the same operation. It is not intended that this test method be a substitute for Test Method D 943 or be used to compare the service lives of new oils of different compositions.

4.2 This test method is also used to assess the remaining oxidation test life of in-service oils.

NOTE 2—A modification of the rotating vessel method has been published as Test Method D 2112, which uses a similar procedure and apparatus but a lower (140°C) bath temperature. Test Method D 2112

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.09 on Oxidation.

Current edition approved June 10, 1998. Published November 1998. Originally published as D 2272-64 T. Last previous edition D 2272-91.

<sup>2</sup> von Fuchs, G. H., Claridge, E. L., and Zuidema, H. H., "The Rotary Bomb Oxidation Test for Inhibited Turbine Oils," *Materials Research and Standards, MTRSA* (formerly *ASTM Bulletin*), No. 186, December 1952, pp. 43-46; von Fuchs, G. H., "Rotary Bomb Oxidation Test," *Lubrication Engineering*, Vol 16, No. 1, January 1960, pp. 22-31.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 02.03.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 06.04.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>6</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>7</sup> *Annual Book of ASTM Standards*, Vol 10.03.

<sup>8</sup> *Annual Book of ASTM Standards*, Vol 05.02.

<sup>9</sup> *Annual Book of ASTM Standards*, Vol 05.03.

<sup>10</sup> *Annual Book of ASTM Standards*, Vol 14.03.

<sup>11</sup> Available from British Standards Institute, 2 Park St., London, England W1A2BS.

<sup>12</sup> Available from Institute of Petroleum, 61 New Cavendish St., London, W. I., England.

requires duplicate testing and Test Method D 2272 conducted duplicate testing in the past.

## 5. Apparatus

5.1 *Oxidation Vessel, Glass Sample Container with Four-Hole PTFE Disk, Hold-Down Spring, Catalyst-Coil, Pressure Gage, Thermometer, and Test Bath*, as described in Annex A1. The assembled apparatus is shown schematically in Fig. 1 and Fig. A1.6.

## 6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications for analytical reagent grade chemicals where such specifications are available.<sup>13</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Isopropyl Alcohol* (**Warning**—Flammable. Health hazard.), 99 % refined, conforming to Specification D 770.

6.3 *Liquid Detergent*.

6.4 *n-Heptane* (**Warning**—Flammable. Health hazard.), 99.0 minimum mol % (pure grade).

6.5 *Oxygen*—99.5 %, with pressure regulation to 620 kPa (90 psi, 6.2 bar). (**Warning**—Vigorously accelerates combustion.)

6.6 *Potassium Hydroxide, Alcohol Solution (1 %)*—Dissolve 12 g of potassium hydroxide (KOH) pellets in 1 L of the isopropyl alcohol. (**Warning**—Flammable. Health hazard.)

6.7 *Silicone Carbide Abrasive Cloth*, 100-grit with cloth backing.

6.8 *Silicone Stopcock Grease*.

6.9 *Wire Catalyst, Electrolytic Copper Wire*,  $1.63 \pm 1\%$  mm ( $0.064 \pm 1\%$  in.) in diameter (No. 16 Imperial Standard Wire Gage or No. 14 American Wire Gage, 99.9 % purity, conforming to Specification B 1. Soft copper wire of an equivalent grade may also be used.

6.10 *Petroleum Spirit*, (**Warning**—Combustible. Health hazard.) Conforming to Specification D 235 for petroleum spirit (mineral spirits).

6.11 *Acetone*, (**Warning**—Flammable. Health hazard.) Conforming to Specification D 329).

6.12 *Reagent Water*, conforming to Specification D 1193, Type II.

## 7. Sampling

7.1 Samples for this test method can come from tanks, drums, small containers, or even operating equipment. Therefore, use the applicable apparatus and techniques described in Practice D 4057.

## 8. Preparation of Apparatus

8.1 *Catalyst Preparation*—Before use, polish approximately 3 m of the copper wire with a silicon carbide abrasive cloth and wipe free from abrasives with a clean, dry cloth. Wind the wire into a coil having an outside diameter 44 to 48 mm and weight of  $55.6 \pm 0.3$  g and stretched to a height of 40 to 42 mm. Clean the coil thoroughly with isopropyl alcohol, air-dry, and insert inside the glass sample container by a turning motion, if necessary. A new coil is used for each sample. For extended storage, the prepared coil may be packaged in a dry, inert atmosphere. For overnight storage (less than 24 h), the coils may be stored in *n*-heptane.

NOTE 3—Commercially available and prepackaged coils prepared as described in 8.1 can also be used for the test.<sup>14</sup>

<sup>14</sup> Prepackaged coils were provided for Spring 1995 round robin.

<sup>13</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U. S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

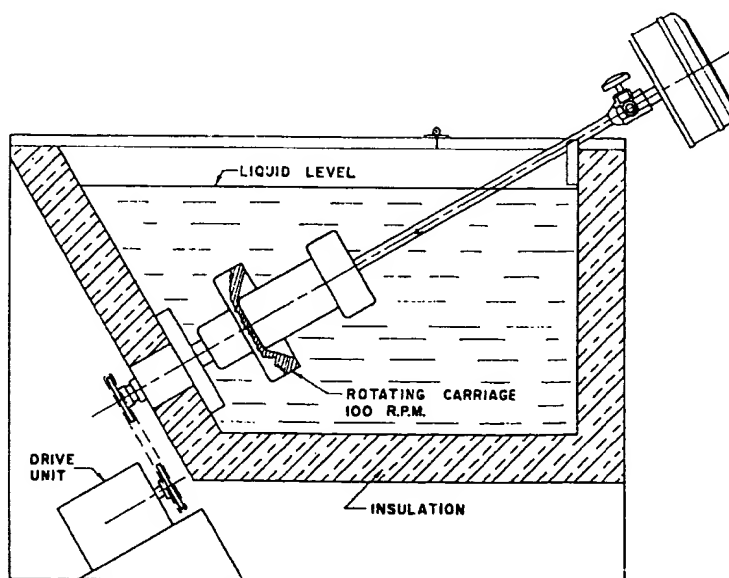


FIG. 1 Schematic Drawing of the Rotary Vessel Test Apparatus



**8.2 Cleaning of Vessel**—Wash the vessel body, cap, and inside of vessel stem with hot detergent solution and rinse thoroughly with water. Rinse the inside of the stem with isopropyl alcohol and blow dry with clean compressed air. If the vessel body, cap, or inside of the stem smells sour after simple cleaning, wash with 1 % alcoholic KOH solution and repeat as before.

**NOTE 4—Caution:** Failure to remove oxidation residue can adversely affect test results.

**8.3 Cleaning of Glass Container**—Drain and rinse with a suitable solvent (for example, petroleum spirit or acetone). Soak or scrub in an aqueous detergent solution. Brush thoroughly and flush thoroughly with tap water. Rinse with isopropyl alcohol, followed by distilled water and air dry. If any insolubles remain, soak overnight in an acid-type cleaning solution and repeat the above procedure starting from the tap water flush.

**8.4 Cleaning of Polytetrafluoroethylene (PTFE) Disk**—Remove any residual oil with a suitable solvent and clean by brushing with detergent solution. Rinse thoroughly with tap water, followed by distilled water rinse and air dry.

## 9. Procedure

**9.1 Charging**—Weigh the glass sample container with a freshly cleaned catalyst coil. Weigh  $50 \pm 0.5$  g of oil sample into the container; also add 5 mL of reagent water. Add another 5 mL of reagent water to the vessel body and slide and the sample container into the vessel body (see Note 5). Cover the glass container with a 57.2-mm (2 1/4 in.) PTFE disk and place a hold-down spring<sup>15</sup> on top of the PTFE disk. Apply a thin coating of silicone stopcock grease to the O-ring vessel seal located in the gasket groove of the vessel cap to provide lubrication, and insert the cap into the vessel body.

**NOTE 5**—The water between the vessel wall and the sample container aids heat transfer.

**9.1.1** Tighten the closure ring by hand. Cover the threads of the gage-nipple with a thin coating of stopcock grease (PTFE pipe tape is a suitable alternative to the use of stopcock grease) and screw the gage into the top center of the vessel stem. Attach the oxygen line with an inline pressure gage to the inlet valve on the vessel stem. Slowly turn on the oxygen supply valve until the pressure has reached 620 kPa (90 psi, 6.2 bar). Turn off the oxygen supply valve. Slowly release pressure by loosening the fitting or by using an inline bleeder valve. Repeat purging process two more times; purge step should take approximately 3 min. Adjust the regulating valve on the oxygen supply tank to 620 kPa (90 psi, 6.2 bar) at a room temperature of 25°C (77°F). For each 2.0°C (3.6°F) above or below this temperature, 5 kPa (0.7 psi, 0.05 bar) shall be added or subtracted to attain the required initial pressure. Fill the vessel to this required pressure and close the inlet valve securely by hand. If desired, test the vessel for leaks by immersing in water (see Note 6).

**NOTE 6**—If the vessel was immersed in water to check for leaks, dry the

outside of the wet vessel by any convenient means such as airblast or a towel. Such drying is advisable to prevent subsequent introduction of free water into the hot oil bath which would cause sputtering.

**9.2 Oxidation**—Bring the heating bath to the test temperature while the stirrer is in operation. Switch off stirrer, insert the vessel into the carriages, and note the time. Restart the stirrer. If an auxiliary heater is used, keep it on for the first 5 min of the run and then turn it off (see Note 7). The bath temperature shall stabilize at the test temperature within 15 min after the vessel is inserted. Maintain the test temperature within  $\pm 0.1^\circ\text{C}$  (see Note 8).

**NOTE 7**—The time for the bath to reach the operating temperature after insertion of the vessel may differ for different apparatus assemblies and should be observed for each unit. The objective is to find a set of conditions that does not permit a drop of more than 2°C after insertion of the vessel and allows the vessel pressure to reach a plateau within 30 min as shown in Curve A of Fig. 2.

**NOTE 8**—Maintaining the correct temperature within the specified limits of  $\pm 0.1^\circ\text{C}$  during the entire test run is an important factor assuring both repeatability and reproducibility of test results.

**9.3** Keep the vessel completely submerged and maintain continuous and uniform rotation throughout the test. A standard rotational speed of  $100 \pm 5$  rpm is required; any appreciable variations in this speed could cause erratic results.

**9.4** The test is complete after the pressure drops more than 175 kPa (25.4 psi, 1.75 bar) below the maximum pressure (see Note 9). The 175 kPa pressure drop usually, but not always, coincides with an induction-type *period of rapid pressure drop*. When it does not, the operator may question whether he has produced a valid experiment (see Note 10).

**NOTE 9**—While termination of the test at a 175 kPa (25.4 psi, 1.75 bar) pressure drop is the standard procedure, some operators may elect to stop the test at lesser pressure drops or to observe the condition of the oil after a predetermined test period of perhaps 100 min; that is, well within the normal induction period of new inhibited oils.

**NOTE 10**—A typical experiment is shown in Fig. 2 as Curve A. The maximum pressure is expected to be reached within 30 min, a pressure plateau is established, and an induction-type pressure drop is observed. Curve B, in which there is a gradual decrease in pressure before the induction break is recorded, is more difficult to evaluate. The gradual decrease in pressure could be due to a vessel leak; although some synthetic fluids will generate this type of curve. If a leak is suspected, repeat the test in a different vessel. If the same type of curve is derived when the test is repeated, the experiment is likely valid.

**9.5** After termination of the test, the vessel shall be removed from the oil bath and cooled to room temperature. The vessel can be briefly dipped into and swirled around in a bath of light mineral oil to wash off the adhering bath oil. The vessel is rinsed off with hot water, then immersed into cold water to quickly bring it to room temperature. Alternately, the vessel can be cooled to room temperature in air. The excess oxygen pressure is bled off and the vessel opened.

## 10. Report

### 10.1 Interpretation of Results:

**10.1.1** In reference to Fig. 2, Curve A, observe the plot of the recorded pressure versus time and establish the plateau (see Note 10). Record the time at the point on the falling part of the curve where the pressure is 175 kPa (25.4 psi, 1.75 bar) less than the established plateau pressure. If the test is repeated, the

<sup>15</sup> PTFE disk with 4-holes and hold down spring were provided for Spring 1995 round robin.

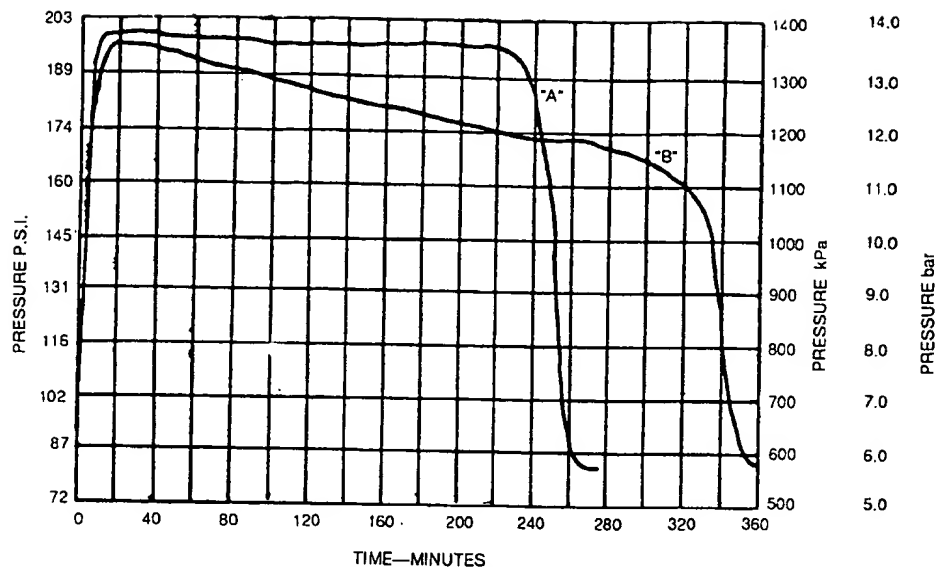


FIG. 2 Pressure Versus Times Plot of Two Rotary Vessel Oxidation Test Runs

plateau pressures in repeat tests should not differ by more than 35 kPa (5.1 psi, 0.35 bar).

10.1.2 In reference to Fig. 2, Curve B, observe the plot of the recorded pressure versus time and establish the maximum pressure obtained during the initial 30 min of the experiment (see Note 10). Record the time on the falling part of the curve where the pressure is 175 kPa (25.4 psi, 1.75 bar) less than the established maximum pressure. If the test is repeated, maximum pressures in repeat tests should not differ by more than 35 kPa (5.1 psi, 0.35 bar).

#### 10.2 Report the Results:

10.2.1 In reference to Fig. 2, Curve A, the vessel life of the sample is the time in minutes from the start of the test to a 175 kPa (25.4 psi, 1.75 bar) pressure drop from the level of the established plateau.

10.2.2 In reference to Fig. 2, Curve B, the vessel life of the sample is the time in minutes from the start of the test to a 175 kPa (25.4 psi, 1.75 bar) pressure drop from the maximum pressure.

NOTE 11—In reporting test results, it is recommended that it be indicated whether tests were made with stainless steel or chrome-plate copper vessels.

### 11. Precision and Bias <sup>16</sup>

11.1 The precision and bias statement is generated from the

<sup>16</sup> Supporting data are provided in Supplement I. They are also available from ASTM headquarters by requesting RR:D02-1409.

research report (95 % confidence). The data range of results in RR:D02-1409 is from 30 to 1000 min.

11.1.1 *Repeatability*— The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

$$0.12 X \quad (1)$$

where  $X$  denotes mean value.

11.1.2 *Reproducibility*— The difference between two single and independent results obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

$$0.22 X \quad (2)$$

where  $X$  denotes mean value.

NOTE 12—This precision statement was prepared with data on seven oils (an uninhibited base oil and three new and three used steam turbine oils) tested by eleven cooperators. The oils covered values in the ranges from 30 to 1000 min. Oils with results greater than 1000 min exhibited poor precision in the Spring 1995 round robin.

11.2 *Bias*—There being no criteria for measuring bias in these test-product combinations, no statement of bias can be made.

ANNEX

(Mandatory Information)

A1. APPARATUS FOR ROTARY PRESSURE VESSEL OXIDATION TEST

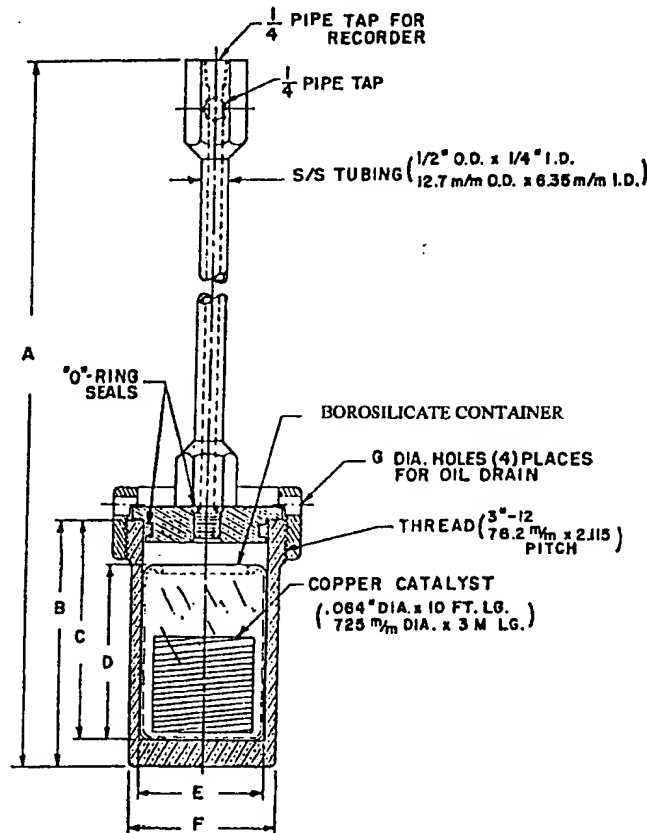
A1.1 *Oxidation Vessel*, with body, cap, closure ring, and stem, constructed as shown in Figs. A1.1-A1.4.

A1.1.1 *Vessel Body and Cap*, shall be constructed of 18-8 or 321S12/321S20 Part 1 (BSI) stainless steel to ensure a proper rate of heat transfer. The interior surface shall be given a smooth finish to facilitate cleaning. Alternatively, the vessel

body and cap may be machined from 76.2 mm (3 in.) solid copper rod and then heavily chrome plated.

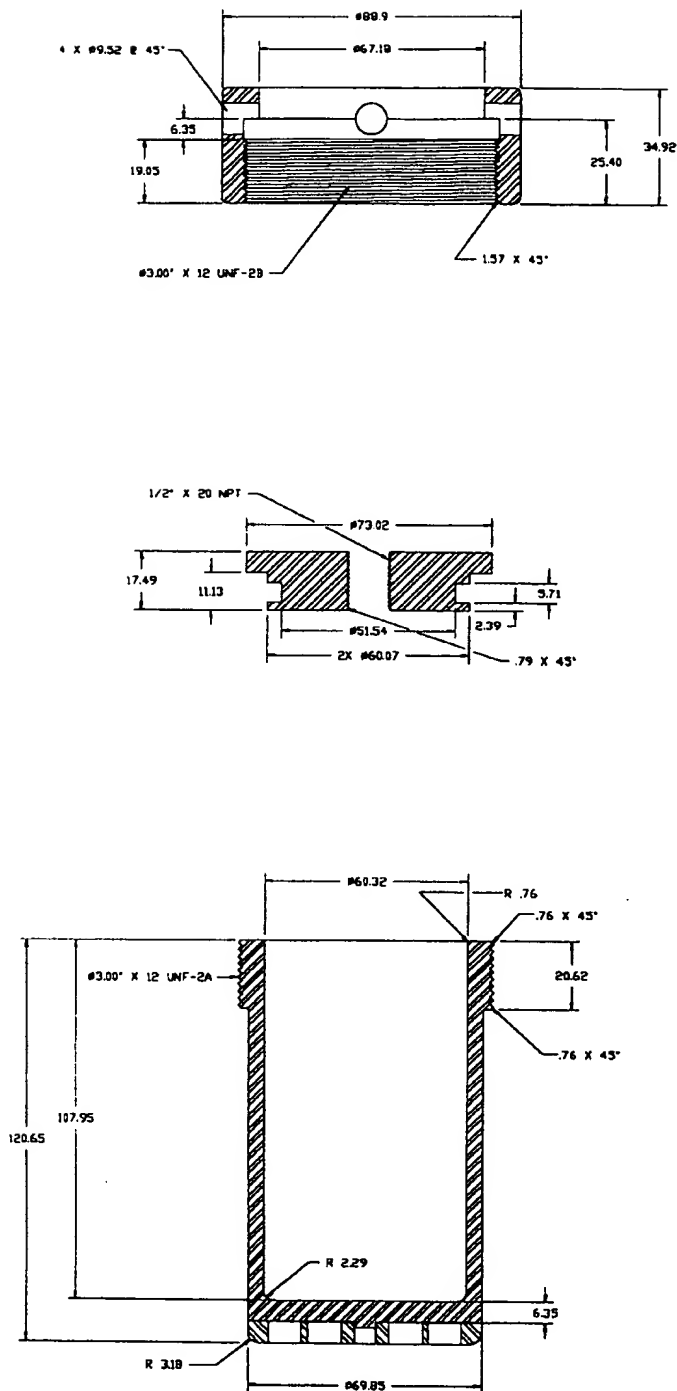
A1.1.2 *Vessel Stem*, shall be constructed of stainless steel, the stem having an inside diameter of 6.4-mm (1/4-in.) and shall be equipped with a 6.4 mm (1/4-in.) needle valve.

A1.1.3 *Closure Ring*, shall be made of chrome-plated steel



	Inches	Millimeters
A	21 1/8	538.58
B	4 3/4	120.65
C	4 1/4	107.95
D	3 3/8 to 3 1/2	80 to 89
E	2.375 (+0.010 / -0.000)	60.325/60.570
F	2 3/4	69.85
G	3/8	9.525

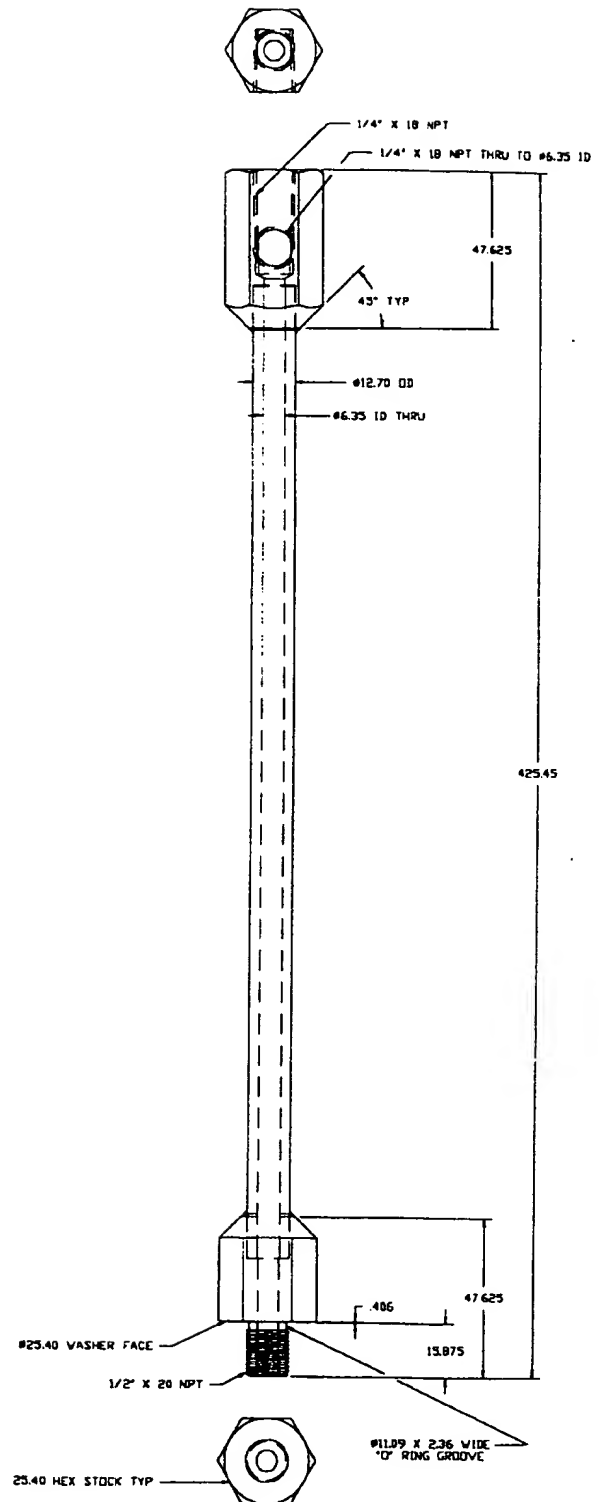
FIG. A1.1 Oxidation Vessel



Unless otherwise specified all dimensions in millimeters.

NOTE—The vessel shown in Figs. A1.1 and A1.2 can also be used for Test Method D 4742 (TFOUT). Test Method D 2272 and IP 229 utilize different drive mechanisms for the for the vessel; hence, US and UK vessels/baths are not interchangeable.

FIG. A1.2 Construction of Oxidation Vessel



or chrome-plated aluminum bronze BS 2032.

A1.1.4 The vessel shall withstand a working pressure of

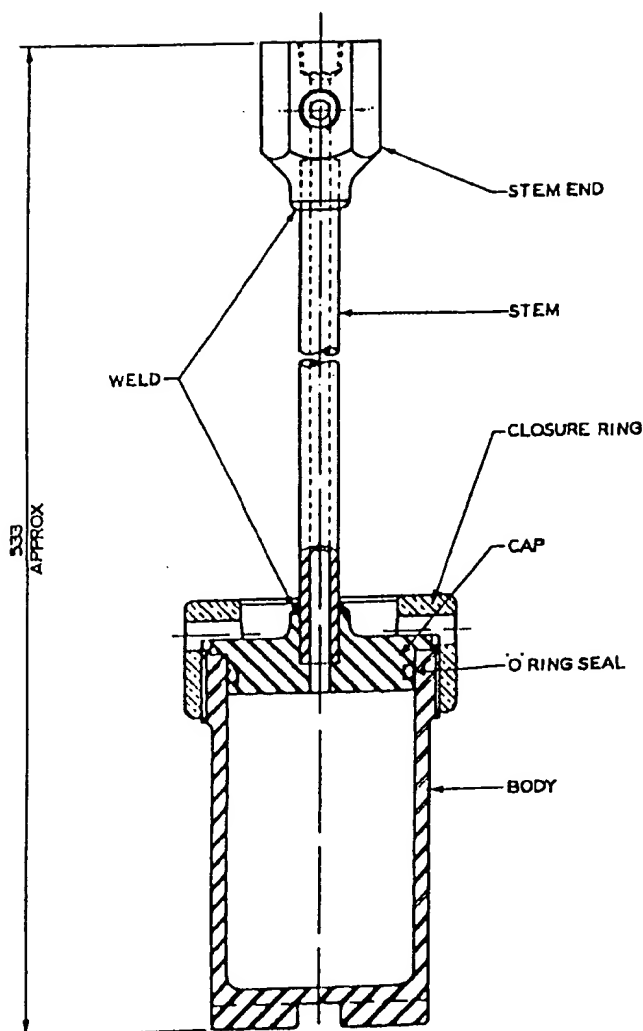


FIG. A1.3 Oxidation Vessel

3450 kPa (500 psi, 34.5 bar) at 150°C.

A1.1.5 *O-ring Gaskets*, Viton or silicon, 50.8-mm (2-in.) in inside diameter by 60.3-mm (2 3/8-in.) in outside diameter (BS/USA size No. 329). Caps with larger seal recess diameters will require 54 mm (2 1/8 in.) inside diameter by 60.3-mm (2 3/8-in.) in outside diameter (BS/USA size No. 227).

A1.2 *Glass Sample Container*, with copper catalyst coil, 175-mL capacity as shown in Fig. A1.5 constructed of borosilicate glass. Glass sample container shall have a sliding fit in the vessel with no excess side clearance. The container alone shall have a maximum wall thickness of 2.5 mm and shall weigh no more than 100 g.

A1.2.1 *Top of Sample Container*, shall be covered with 57.2-mm (2 1/4-in.) diameter PTFE disk. The disk will have

four 3.2-mm (1/8-in.) diameter holes evenly spaced in a 9.5-mm (3/8-in.) radius from the center of the disk. The disk shall have a thickness of 1.6-mm (1/16-in.). A stainless steel hold-down spring as shown in Fig. A1.6 shall be used to ensure rotation of the sample container. The assembly is shown in Fig. A1.7.

### A1.3 Recording Devices:

A1.3.1 *Recording Gage*<sup>17</sup>, as shown in Fig. A1.8 or indicating, with a range from 0-1400 kPa (or 0 to 200 psi or 0 to 14 bar) and graduated in 25-kPa (or 5 psi or 0.25 bar) divisions. The accuracy shall be 2.5 % or less of the total scale interval. Recording gages should be mounted so that the face is perpendicular to the axis of rotation.

A1.3.2 *Pressure Measurement System*, consisting of electronic pressure transducers, power source, mounting equipment and connecting cables. The rotary transducer couplings can be mounted directly on the vessel stem in place of the standard mechanical pressure recorders. The pressure transducer shall have a span of 0 to 1400 kPa (or 0 to 200 psi or 0 to 14 bar). The accuracy should be valid over a wide compensated temperature range. The output signal from the transducer can be channeled into a datalogger, microprocessor based recorder, or a computer for data acquisition. The data acquisition package should be capable of logging pressure data vessel time. The overall system accuracy of the data should be within 2.5 % of the total scale.

A1.4 *Oxidation Bath*, equipped with an efficient stirrer and with a suitable device from holding and rotating the vessel axially at an angle of 30° at 100 ± 5 rpm while submerged in oil to a point at least 25 mm (1 in.) below the level of the bath liquid.

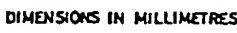
A1.4.1 At bath at least 230 mm (9 in.) deep, filled with 30 L (8 gal) of heavy bath oil per vessel, has the proper heat capacity. Silicone oil, it shall be necessary to house the oil bath under a fume hood to contain any oil vapor generated.

A1.4.2 Provide thermal regulation to maintain the bath within 0.1°C of the test temperature. There should be sufficient, immediately available heat to bring the bath to operating temperature within 15 min after the vessels have been inserted.

A1.5 *Thermometer*, IP 37C sludge test thermometer having a range from 144 to 156°C graduated in 0.2°C intervals or other temperature measuring device, having an accuracy of 0.1°C.

A1.6 *Gage*, for pressurizing vessel to 620 kPa (90 psi) graduated in 1.5 kPa (0.2 psi) increments.<sup>17</sup>

<sup>17</sup> Heise gage, Model CM has been found satisfactory for this purpose. Available from Dresser Industries, 153 South Main St., Newtown, CT 06470.



**FIG. A1.4 Details of Oxidation Vessel**

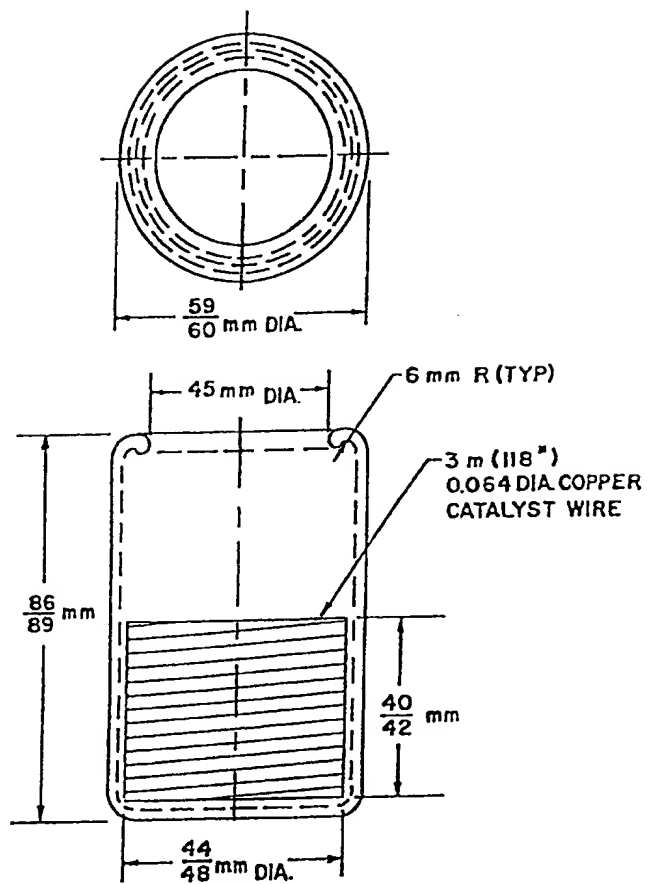
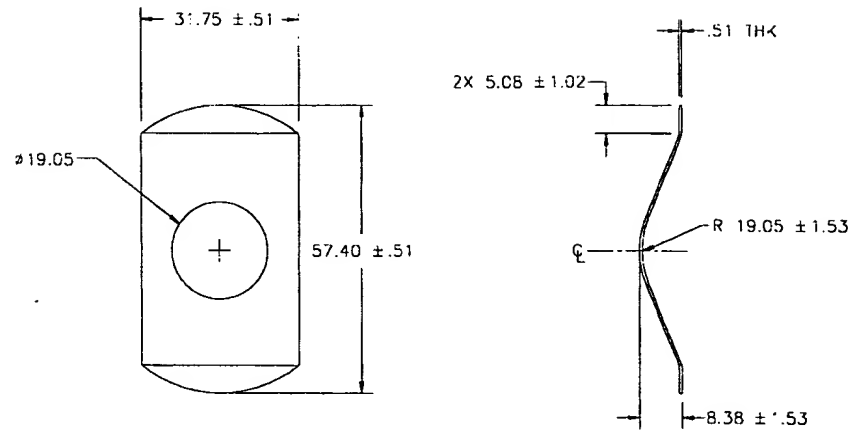


FIG. A1.5 Borosilicate Glass Sample Container



All dimensions are in millimeters  
Unless otherwise specified tolerance is  $\pm .13$

**FIG. A1.6 Hold-down Spring**



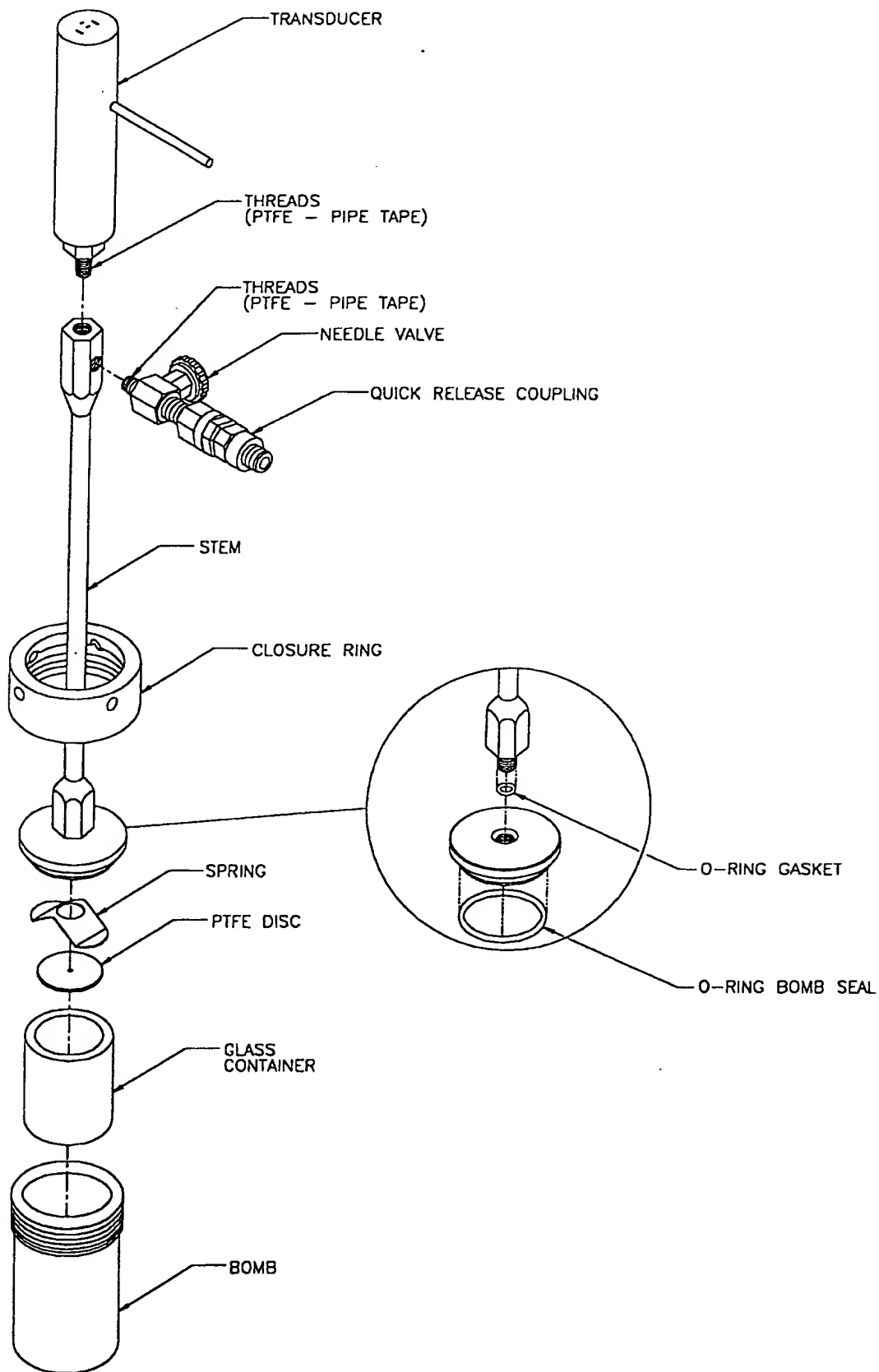


FIG. A1.7 Oxidation Vessel Assembly

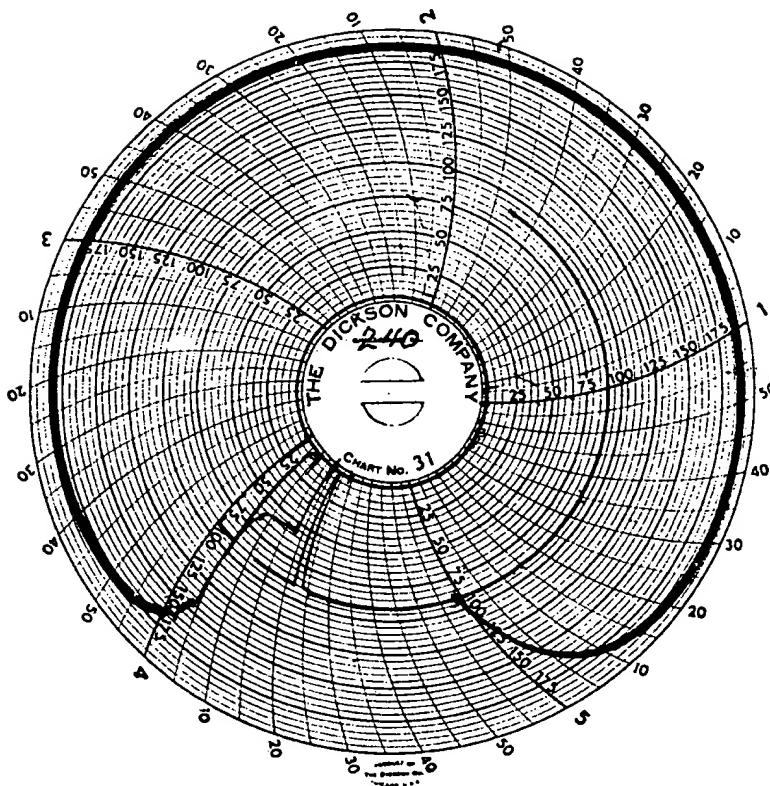


FIG. A1.8 Chart of Recording Pressure Gage (Actual Size = 4½ in.)

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# Evaluation of Some Poly-Alpha-Olefins in a Pressurized Penn State Microoxidation Test<sup>©</sup>

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*A pressurized modification of the Penn State microreactor has been tested and compared with the atmospheric pressure unit. The partial pressure of oxygen has been kept constant by using a 4:1 mole ratio of nitrogen to air.*

*Evaporation effects have been compared for two low-volatility PAO base oils containing PAN. While some problems still exist in the pressurized unit, the reduced evaporation allows a comparison of additive effectiveness in two PAO base oils differing only in degree of saturation. Residual evaporation losses in the pressurized unit are attributed to the valve and pressure gauge which are not heated. A combination of volatile PAN and nonvolatile ZDDP have also been studied and exhibit lesser differences between the two PAO base oils. The less saturated PAO shows somewhat less oxidative stability. Additional short time tests have been conducted with the combined inhibitor package and the results evaluated by gel permeation chromatography using an ultraviolet detector. Large initial differences were noted between the unsaturated and the saturated fluids. This procedure shows promise for base oil evaluations.*

## INTRODUCTION

A large number of bench tests for the study of the oxidative stability of lubricants have been developed (1). These test procedures fall into four categories:

1. Isothermal bulk oxidation tests where conventional property changes due to oxidation are measured on the residual sample (2)–(6).
2. Nonisothermal bulk tests where the test fluid is circulated over a hot surface from a lower temperature reservoir and deposits formed on the hot surface are measured (7)–(10).
3. Oxidation tests where oxidation is determined indirectly by system pressure change (11), chemiluminescence (12) or free radical titration (13).

4. Thin film test methods with varying degrees of analysis e.g., DSC (14), TGA (15), TFOUT (16), and the Penn State microoxidation test (17). Of these tests, the microoxidation test uses the most comprehensive chemical analysis.

All four test categories have been used as a basis for oxidative testing of automotive crankcase lubricants and subsequent correlation with engine tests. All of the general test categories have advantages as well as limitations. The primary limitation of bulk oxidation tests is the severe diffusion limitations involved in providing oxygen for the reaction. The nonisothermal oxidative tests may be better for simulating such conditions in an engine, but the deposit ratings depend on adherence of the sludge and decomposition products to the hot surface. Where oxidation severity is determined by a pressure change, the pressure buildup of oxidation products and oxygen diffusion limitations are difficult to determine as correction factors.

The thin film methods appear to have the most promise for the evaluation of oxidative deterioration of lubricants. Film thickness can be controlled to reduce or eliminate oxygen diffusion limitations. The onset of oxidation can generally be detected as a function of time in the TFOUT, DSC, and TGA units. In the case of the Penn State microoxidation test, induction period is detected only by end-of-test chemical analyses. The Penn State microoxidation test is described in detail by Cvitkovic et al (17). End-of-test analyses can describe the products as a function of molecular size (GPC) (18); chemical class or bonding (IR) (19); chemical groupings (NMR) (18); deposit formation (microbalance) (20); or metal surface-lubricant interaction (AAS) (21). The rate of reaction can be measured by conventional GPC analysis to determine the kinetics of the reactions (22). These readily measured properties of oxidizing systems have been shown to correlate well with III-C and III-D engine sequence tests using ASTM reference oils (23).

The Penn State microoxidation test has a substantial volatility or evaporation component. Since the oxidation of a lubricant is controlled by kinetics while evaporation is a mass transfer function, the modeling of oxidation in the microoxidation test is complicated (22), (24). The fact that many

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effective oxidation inhibitors are more volatile than the base oil makes stable life studies as a function of additive type and concentration difficult. This is particularly true in a fully compounded automotive lubricant where the dispersant, detergents, and zinc dithiophosphate oxidation inhibitor and antiwear additive are all relatively nonvolatile. Many supplemental oxidation inhibitors that are added to motor oils for additional stability are volatile and may be preferentially lost in any thin film oxidation test.

To minimize this volatility problem with base oils, as well as additive packages, the Penn State microoxidation test has been modified to run under an applied pressure, thereby reducing the rate and amount of volatility losses. This pressurized modification of the Penn State microoxidation test is the subject of this paper. The ability to detect small impurities not adequately controlled by oxidation inhibitors and to measure the stable life or induction period with volatile oxidation inhibitors are illustrated using poly-alpha-olefin base oils.

## TEST APPARATUS AND PROCEDURE

The Penn State pressurized test apparatus is shown in Fig. 1. This system consists of a 38.1 mm OD stainless steel cylinder equipped with a valve and a pressure gauge [Fig. 1(a)]. The flanged joint contains a silicone rubber O-ring seal which allows for repeated use at temperatures up to 275°C. The metal catalyst test cup is placed at the bottom of a glass liner [Fig. 1(b)]. A small quantity (20–40  $\mu$ l) of fluid is then injected onto the metal catalyst test cup. The glass liner is covered with a loose-fitting glass lid and then inserted into the stainless steel cylinder. The glass lid is used to prevent liquid condensate from returning to the area of the test cup. The system is then sealed.

The unit which already contains 1 atm of air is pressurized to 60 psig with nitrogen. This provides the same partial pressure of oxygen found in the atmospheric test. The reactor top excluding the gauge is wrapped with heating wire (2 ohms/ft) and insulating tape to maintain a uniform temperature throughout the entire assembly during the test.

To begin an experiment, the heating wire is connected to a variable transformer and the reactor is immersed in a constant-temperature, molten-metal bath. The heating cycle for the test apparatus is determined by placing thermocouples on the metal catalyst test cup, as well as in the top of the unit. The heat-up time for a given run is subtracted from the overall test time to determine the test time at the desired test temperature. The measured heat up time for a test at 225°C is 7 minutes. In this paper, the test time shown is the time the system was at the operating temperature.

During the initial heat-up period, the pressure increases rapidly to 90–100 psig, depending upon the reaction temperature. At the end of the chosen test time, the reactor is removed from the molten metal bath and cooled rapidly by a high-velocity stream of cold air. When the reactor reaches room temperature, the pressure is released and the unit is disassembled for further analysis.

The fluid remaining on the catalyst surface is diluted with tetrahydrofuran and analyzed with gel permeation chro-

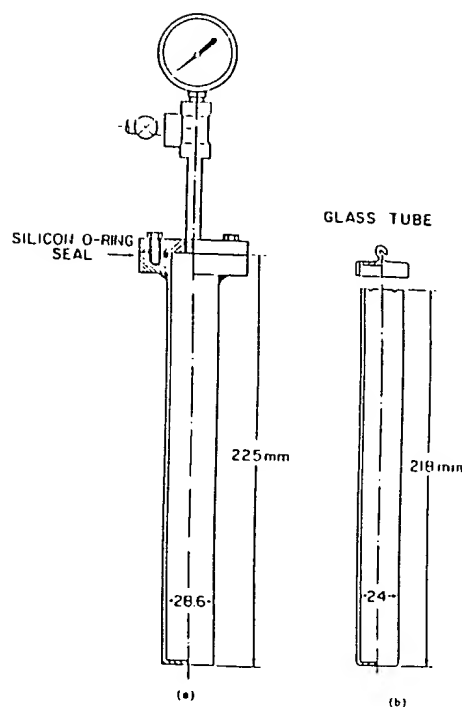


Fig. 1—Pressure system microoxidation test apparatus

matography, performed on a unit with differential refractive index and ultraviolet light absorption detectors.

Evaporation tests in the pressurized system can be done by evacuating the unit using a water aspirator and pressurizing it with nitrogen. These evacuation and pressurizing steps are repeated three times to minimize the oxygen remaining in the test system.

There are two principle differences between the atmospheric and the pressurized microoxidation tests. First, the atmospheric test uses a continuous once-through flow system using air, while the pressurized system is a sealed unit which has only internal convection for the gas system circulation. In the sealed system, based on an average molecular weight of 524 for the poly-alpha-olefin fluid used, the oxygen present provides 10.9 moles of oxygen per mole of poly-alpha-olefin fluid. Second, the atmospheric test is started with the test unit at the desired temperature and the test fluid is then added. The fluid is heated in a matter of seconds so that significant tests of 5 minutes duration can be run. In the pressurized system, the total unit containing the test fluid is inserted in a constant temperature bath without preheating. This system requires a heat-up time which is a function of the test temperature and heat capacity of the bath. At 225°C, using a molten-liquid, constant-temperature bath, a heat-up time of 7 minutes is required to reach the test temperature.

## TEST FLUIDS

Two experimental poly-alpha-olefin (PAO) fluids supplied by a commercial producer were used in this study. Properties of a typical commercial quality PAO (Fluid A) are shown in Table 1, as well as those of a more completely hydrogenated PAO with similar molecular weight distribution and viscosity properties (Fluid B). The bromine index of the first fluid is equivalent to about 4.4 percent un-

TABLE 1—PHYSICAL PROPERTIES OF PAO FLUIDS		
FLUID	A	B
Bromine	1325	2
Viscosity in cSt at		
-40°C	8436	7774
-17.8	890	834
40.0	31.0	30.5
100.0	5.8	5.8
Viscosity Index	133	137
Pour Point °C	< -54	< -54
Flash Point °C	246	240
Fire Point °C	274	270
Total Acid Number	<0.03	<0.03
Specific Gravity (15.6/15.6°C)	0.8294	0.8280
Carbon Number %		
C30	30.2	31.3
C40	63.2	59.6
C50	6.6	8.5

saturated material; the second indicates about 0.1 percent unsaturation. A more completely hydrogenated PAO with molecular weight distribution and viscosity properties similar to those of the commercial sample are also shown in Table 1. The bromine index in this case indicates about 0.1 percent unsaturation.

Two additive packages were used in these studies. For the stable life studies, 1.0 percent phenyl alpha naphthylamine (PAN) was added to each of the PAO test fluids. The second additive package consisted of 0.5 weight percent PAN plus 1.88 percent zinc dialkyldithiophosphate (ZDDP). This additive package was used with the two PAO oils for oxidation stability evaluation as well as stable life studies.

## INTERPRETATION OF GPC CHROMATOGRAMS

The refractive index chromatograms of PAO fluids are used to show the quantitative distribution of initial and final products by molecular size from the evaporation and oxidation tests. The chromatogram obtained for the oxidation of Fluid B inhibited with 1 percent PAN at 225°C is shown in Fig. 2. The chromatogram for the oxidized fluid reflects the loss of original PAO and inhibitor by evaporation and the production of material of higher molecular weight than that of the original PAO fluid by oxidation. The molecular size of the oxidation products shown in Fig. 2 is based on the elution time for a polystyrene of equivalent molecular weight. The rate of depletion of the original PAO basestock, as well as the rate of formation of high-molecular-weight products is obtained by measuring the appropriate areas under the curve. These areas are compared to the area generated by the original sample, thereby giving weight percentages of material in the same molecular size as the original sample, reacted material of a different molecular size, and by difference the amount of material lost by evaporation.

Formation of incipient oxidation products which cannot be detected by RI analysis can be observed with ultraviolet absorbance. Also, the depletion rate of the inhibitor can be

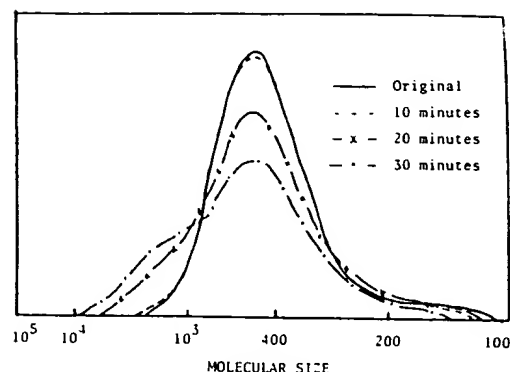


Fig. 2—GPC analysis of PAN inhibited PAO oxidation at 225°C in the atmospheric pressure microoxidation test. Fluid B; catalyst = low carbon steel; PAN conc. = 1.0 Wt. %; GPC = refractive index

obtained from the UV chromatogram by measuring the area under the PAN peak which appears at a molecular size range of 200. Figure 7 shows a typical UV chromatogram of an oxidized PAO fluid sample displaying incipient oxidation product formation. UV absorbance response at a molecular weight of greater than 400 represents oxidation product generation. The UV detector is set at a fixed wavelength of 254 nm. This wavelength gives strong absorption sensitivity to conjugated double bond systems as well as carbonyl groups. These functional groups are found to be general products of oxidation for hydrocarbon structures containing C-C single bonds (19).

## ATOMIC ABSORPTION ANALYSIS

Soluble iron in the oxidized product was measured by atomic absorption spectroscopy (AAS). Oxidized samples were prepared for AAS analysis by dilution with pyridine. Iron concentration was obtained by comparison of sample absorption with absorption from 0.5–10 ppm iron standards.

## RESULTS AND DISCUSSION

The pressurized microoxidation test has been evaluated and compared with the atmospheric pressure microoxidation test using two PAO fluids with and without oxidation inhibitors. The two alpha olefin oligomers shown in Table 1 have about the same mixture of hydrocarbons but differ in completeness of hydrogenation of the olefinic double bonds.

A comparison of the GPC analysis of microoxidations at 225°C run on the same PAN inhibited PAO are shown in Figs. 2 and 3. PAN was chosen for the oxidation inhibitor for these studies since it is an effective inhibitor but much more volatile than the PAO base oil. Oxidation of hydrocarbons including PAO appears to proceed through a peroxy radical to produce an oxidized material with about the same molecular size and volatility as the starting material. This primary oxidation product then reacts much more rapidly than in the primary oxidation step to form a condensation polymer of larger size than the original PAO. The data shown on Fig. 2 indicate that after 10 minutes the inhibitor is still functioning to prevent oxidation and con-

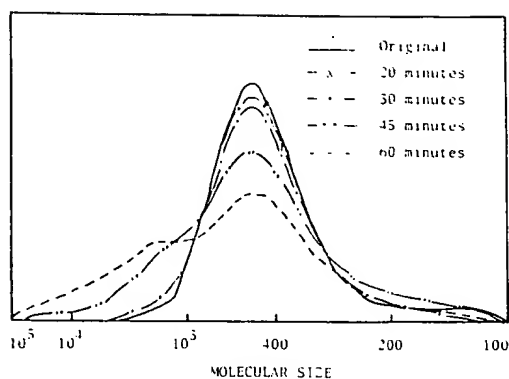


Fig. 3—GPC analysis of PAO oxidation at 225°C in the pressurized microoxidation test.

Pressure = 1 atm air + 4 atm N<sub>2</sub>; Fluid B; catalyst = low carbon steel; PAN = 1.0 Wt. %;  
GPC = refractive index

densation polymerization in the atmospheric pressure unit. The 20- and 30-minute tests, however, show significant oxidation indicating evaporation and/or oxidative destruction of the PAN. Previous tests with white oil have shown that the loss of PAN at 225°C is predominantly by evaporation. In Fig. 3, using the pressurized system, the inhibiting effect of PAN can be seen after 30 minutes test time. That is, the apparent life of the PAN has been increased by a factor of 3 in the pressurized system. The 45- and 60-minute tests show that the inhibitor has become ineffective due to a combination of volatility and oxidation.

The saturated PAO does not give absorption in the UV spectra. PAN does give a significant level of absorption in the GPC analysis. The UV absorption curve for PAN appears at a molecular size range of 200 compared to the RI response for the PAO which ranges from 300 to 1000. Tracking the disappearance of PAN by the UV absorption in the two different microoxidation tests, the data shown in Fig. 4 were obtained. These data show that, after 10 minutes at 225°C in the atmospheric pressure test using

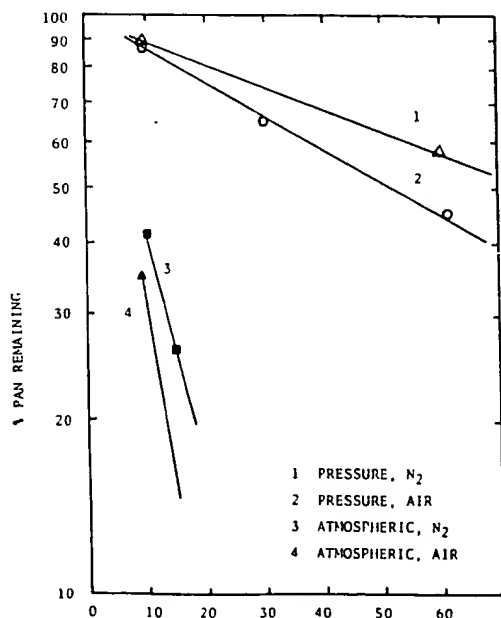


Fig. 4—PAN depletion rates in Fluid B at 225°C

nitrogen gas, about 60 percent of the original PAN has been lost by evaporation. When air is used in the same test conditions, about 65 percent of the PAN is lost. This suggests that evaporation is so severe that the open system is not sensitive enough to measure oxidation stability. The data for the pressurized system show much higher levels of PAN with test time. Only 10 percent of PAN is lost at 10 minutes. In addition, the rate of disappearance of PAN shows a significant difference between nitrogen- and oxygen-containing atmospheres. This difference may be attributed to the amount of the PAN destroyed by oxidation.

These data do suggest that there is a continuing loss of PAN under nitrogen. The best explanation for that loss is the condenser effect of the valve and gauge shown in Fig. 1. The top of the unit, with the exception of the gauge and valve, are heated to about the same temperature of the bulk of the pressure vessel. This problem is believed to be responsible for the scatter of the specific points on the oxidation curves in Figs. 5 and 6.

The effect of PAN as an oxidation inhibitor is shown in Fig. 5. The data in Fig. 4 indicate that, in the pressurized test, the amount of PAN left after 70 minutes of oxidation at 225°C is as high or higher than the PAN concentration after only 10 minutes in the atmospheric test at the same temperature. The data in Fig. 5 show that PAN is still effective in reducing the rate of oxidation after 60-minutes test time. The effectiveness can be judged by the lower slope (reaction rate) of the fluids containing PAN compared with the PAO base oil containing no additives. Data have been presented in previous publications (25) to show an essentially constant reaction rate for the nonadditive hydrocarbons from zero time until more than 60 percent of the initial hydrocarbon molecules become oxidized. Oxidation is in-

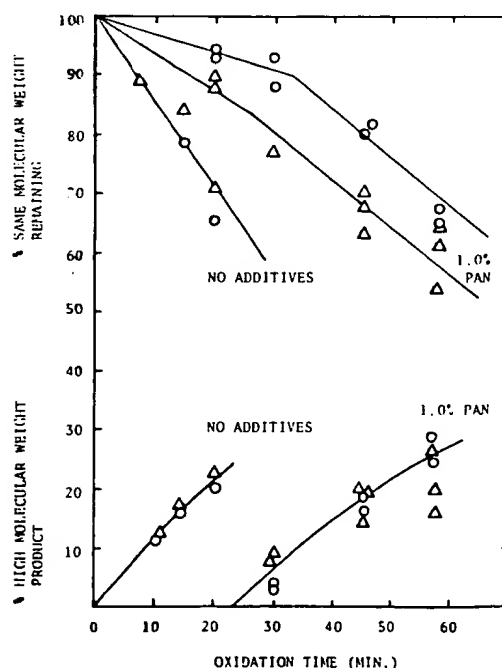


Fig. 5—Additive response of PAO fluids containing 1.0% (Wt.) PAN, test conditions: temperature = 225°C, test pressure = 1 atm air + 4 atm N<sub>2</sub>; catalyst = low carbon steel.

▲ PAO A  
○ PAO B

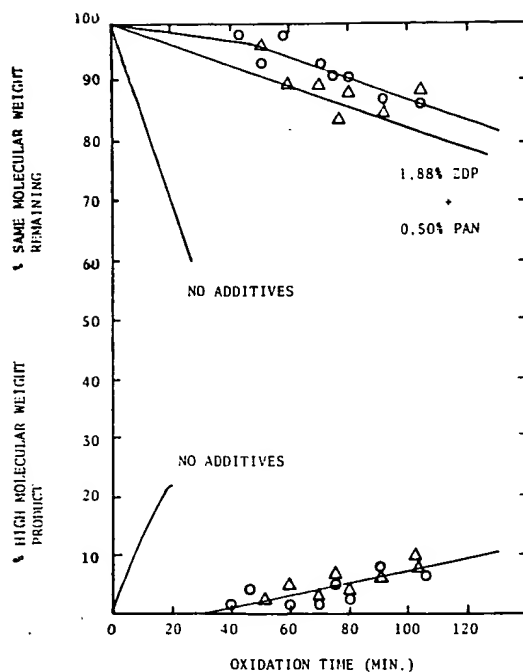


Fig. 6—Additive response of PAO fluids containing 1.88% ZDP + 0.50% PAN.

Test conditions: temperature = 225°C,  
Test pressure = 1 atm air + 4 atm N<sub>2</sub>;  
catalyst = low carbon steel  
▲ PAO A  
○ PAO B

indicated by a decrease in the product remaining in the same molecular weight range as the base oil.

In addition to a decreased oxidation rate due to the presence of PAN, there appears to be a difference in additive effectiveness due to the quality of the PAO base oils. The base oil containing about 4.4 percent unsaturation shows more severe oxidation than the saturated PAO. For both PAO base oils, there appears to be an initial induction period during which the oxidation rate was the lowest. Following this "induction period," the rate increased but was still lower than that of the nonadditive base oils. Another measure of the stable induction period is the delay in the formation of high-molecular-weight oxidized product. For the oxidized PAO base oils, there is somewhat less difference in the high-molecular-weight oxidation curves than for the rate of disappearance of the material having the same molecular weight as the PAOs. It can be noted that the start of high-molecular-weight product formation corresponds to the test time where there is an inflection (increase) in the oxidation rate curve.

The data shown in Fig. 6 are for the two PAO base oils containing 1.88 weight percent ZDDP plus 0.5 weight percent PAN. The concentration of ZDDP is equivalent to that used in some commercial SF/CD automotive lubricants. The ZDDP is a nonvolatile additive and should not be affected by evaporation problems. It can be seen from the data that this additive package is more effective in reducing the oxidation rate as indicated by the reduction of material in the molecular weight range of the PAO base oils. The rate of increase in the amount of high-molecular-weight product (sludge and deposit precursors) is also reduced. The induction period or delay before the production of the high-molecular-weight product is about the same as that noted

with PAN alone. Again, there appears to be a difference in the rate of oxidation caused by the quality of the PAO base oil.

Previous work has shown that soluble iron containing oxidation or corrosion products can catalyze the oxidation reaction. Total iron content of the two oxidized PAO base oils with the additive package is shown in Table 2. These data show that the PAO containing the 4.4 percent unsaturation causes the formation of substantially more soluble iron oxidation or corrosion products. This catalytic effect appears to be the reason for the differences in additive effectiveness in the two PAO base oils. These data suggest that there should be some evidence in the oxidation behavior of the two PAO base oils containing additives that would predict these oxidation and corrosion differences.

Since the analysis of refractive index chromatograms did not show these differences to be large enough to be readily distinguished, some additional studies were done based on short time tests at 225°C. In this case, the ZDDP plus PAN additive package was used and the analysis conducted using a UV chromatogram. The resultant chromatograms are shown as Figs. 7 and 8. In both figures, the solid curve is for the original formulated fluid. The major peak on both figures is for the PAN oxidation inhibitor. In Fig. 8, the small shaded section represents the 4.4 percent unsaturation. In Fig. 7, it can be seen that the first evidence of the formation of high-molecular-weight product indicative of incipient oxidation occurred at 25 minutes. In the case of the PAO with original unsaturation, the 10-minute test shows more oxidized material than the 25-minute test with the saturated PAO. The amount of oxidized material increases rapidly with time for the unsaturated PAO. These data show clearly how the ultraviolet readout on the GPC coupled with the pressurized microoxidation test can show significant differences that cannot be shown based on the refractive index chromatogram. The nonlinear nature of the UV absorption by unsaturated materials formed on oxidation suggest that this technique may be useful in determining small differences in base oil quality.

## CONCLUSIONS

A pressurized modification of the Penn State microoxidation test has been developed to provide better sample

TABLE 2—CORROSION RATES OF CATALYST SURFACE BY OXIDIZING PAO FLUIDS		
Conditions: 225°C		
Pressure System, 1 atm. air + 4 atm. N <sub>2</sub>		
Additives: 1.88% ZDDP plus 0.5% PAN		
Catalyst: Low Carbon Steel		
OXIDATION TIME (MINUTES)	PPM Fe IN PRODUCT MIXTURE	
	FLUID B	FLUID A
10	25	55
20	95	135
25	125	305
30	150	590
35	240	1175
40	705	1540



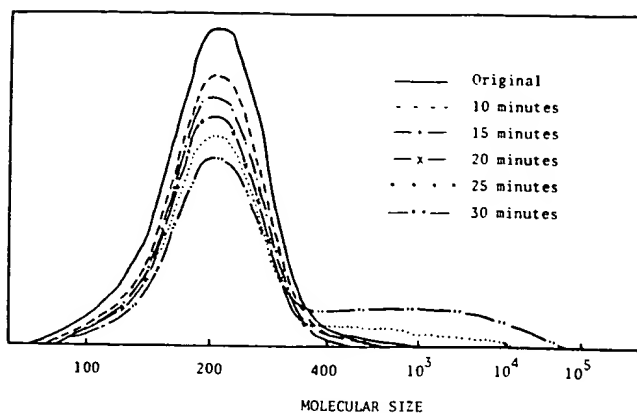


Fig. 7—UV analysis of PAO Fluid B.

Test = pressurized; additives = 0.5 Wt. % PAN + 1.88 Wt. % ZDDP; catalyst = low carbon steel

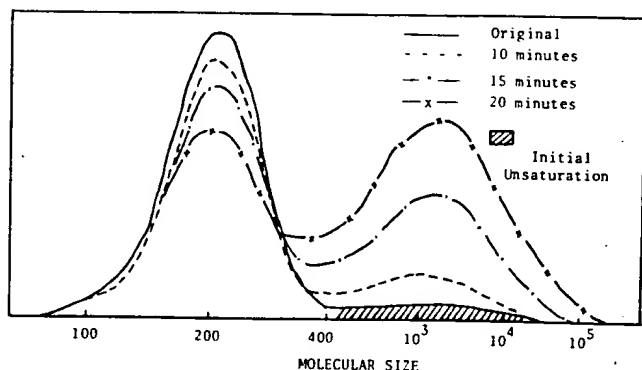


Fig. 8—UV analysis of PAO Fluid A.

Test = pressurized; Additives = 0.5 Wt. % PAN + 1.88 Wt. % ZDDP; catalyst = low carbon steel

retention for volatile fluids and/or additives. The pressurized version uses one atmosphere of air and four atmospheres of nitrogen at room temperature to maintain the same partial pressure of oxygen and, therefore, the same relative severity of this oxidation test and the original test conducted at atmospheric pressure. With the constant temperature bath used for the pressurized test, seven minutes are subtracted from the total time in the constant temperature bath to determine the test time at 225°C.

The improved effectiveness of this test with volatile antioxidants was demonstrated using PAN. Evaporation of PAN under a nitrogen atmosphere at 225°C is reduced by a factor of 12 in the pressurized unit compared with the atmospheric pressure test. For a total test severity of 60 percent of the original PAO lost by evaporation and oxidation, the percentage units lost due to oxidation are less than 5 in the atmospheric pressure test compared with a value of 20 for the pressurized test.

The increased sensitivity of the pressurized microoxidation shows a difference in additive effectiveness of PAN in a saturated PAO compared with the less saturated sample. The differences in stable life can be detected from the amounts remaining in the original molecular weight range, but not by the amounts of high-molecular-weight oxidized product formed from the two PAOs.

A difference in additive effectiveness is still observed for the PAOs containing volatile PAN plus nonvolatile ZDDP.

These differences still indicate that the saturated PAO is the more stable system. In this case, metal oxidation and/or corrosion products show the same trend as the oxidation products. That is, the unsaturated PAO system shows the larger oxidation and corrosion effect on the low carbon steel catalysts providing a larger catalytic effect on the rate of oxidation. The metal-lubricant reaction, in this case, confirms the small difference shown by the refractive index gel permeation chromatograms.

Short time tests designed to evaluate the effectiveness of small amounts of unsaturation on additive response show large differences in an ultraviolet gel permeation chromatogram. These tests show clearly that the olefinic content of the high bromine index PAO is not protected by the PAN and ZDDP inhibitor package.

The pressurized Penn State microoxidation shows a somewhat larger limit of error than the atmospheric test. This difference appears to be related to the condenserlike effect the valve and pressure gauge have when the rest of the unit is heated in the constant temperature bath. Further work will be done to reduce or eliminate this condenser effect.

## ACKNOWLEDGMENT

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